AN ELECTROLYTIC STUDY OF BENZOIN AND BENZIL.[1]

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INTRODUCTION.

A S is well known, there is a wide difference in the action of various oxidizing as well as reducing agents on organic compounds. Probably no better illustration could be given of this than the following, on the oxidation of aniline, from Lassar-Cohn's "Manual of Organic Chemistry:" "With manganese dioxide and sulphuric acid, aniline gives ammonia and very little quinone. Chromic acid mixture gives a quantitative yield of the latter. Potassium permanganate in alkaline solution gives azobenzene, ammonia, and oxalic acid. In acid solution it gives aniline black, which with more energetic oxidation, is converted into quinone. In neutral solution, nitrobenzene and azobenzene are the chief products. Boiling bleaching-powder solution likewise gives nitrobenzene. Hydrogen peroxide in presence of weak acids gives ammonia and dianilidobenzoquinone anilide. In presence of strong acids it seems to give an inuline derivative."

In like manner, there is a marked difference in effect between electrolytic oxygen and hydrogen and other oxidizing and reducing agents. And again, different degrees of oxidation or reduction by the current can be effected by variations in current density, concentration, temperature, etc.

To study the oxidizing and reducing action of the electric current on benzoin and benzil as compared with other agents, and to determine the result of working in different solutions as well as with variations in current density, concentration, and temperature, is the object of this investigation.

The apparatus with which the experiments were performed consisted of a beaker-glass, a porous cup, which separated the anode and cathode liquids, and platinum electrodes, each of 100 sq. cm. surface. When hydrochloric acid solutions were used the platinum anode was replaced by one of carbon.

When heat was applied in sufficient amount to evaporate the

solvent, the top of the porous cup was closed by a rubber stopper, carrying, besides a heavy platinum wire to which was attached the electrode, a tube which led the vapor to a return condenser.

In some of the experiments with alkaline solutions the porous cup was replaced by a bag made of two thicknesses of heavy unbleached muslin, which had been previously soaked in concentrated caustic soda for twenty-four hours.

The outer liquid, whether an oxidation or reduction was being made, consisted of a solution of from ten per cent. to twenty per cent. of the same acid or alkali used in the inner cup.

The solvent generally used throughout this set of experiments was ninety-three per cent. ethyl alcohol. The concentration of the solutions was nearly always kept close to the point of saturation.

The current used for most of the work was that of the ordinary 110 volt incandescent light circuit ; this was regulated by means of lamps and wire resistance, so that any current from one-tenth to ten amperes could be used. In a few instances the current from storage cells was used.

The melting-points given in the following work were taken with an ordinary thermometer and are not corrected.

EXPERIMENTS ON THE ELECTROLYTIC OXIDATION OF TOLUENE.

Before taking up the work on the oxidation and reduction of benzoin, attempts were made to oxidize the methyl group in toluene by the action of electrolytic oxygen. These experiments were unsuccessful, but it is hoped that they may not be without some interest.

The toluene used was from Kahlbaum, and distilled constantly at $110°$.

Experiment I.—

15 grams toluene.	$N.D._{100} = 0.05$ ampere.
210 cc. alcohol.	Voltage $= 60-70$.
15 grams sodium hydroxide.	Temperature, $20°$.
30 cc. water.	Time, 1 hour.

On acidifying the cup contents with hydrochloric acid and filtering off the sodium chloride, the remaining liquid, on distillation, yielded nothing but alcohol, water, and toluene, together with a small amount of brown resin.

Experiment II.—

33 grams toluene.	N.D.$_{100}$ = 0.05 ampere.
460 cc. alcohol.	Voltage = 2$\frac{1}{3}$.
65 cc. water.	Temperature, 25°.
30 grams sodium hydroxide.	Time, 1 hour.

The alcohol was distilled from the anode liquid and hydrochloric acid added to acidulation. This acid liquid, on shaking with ether, gave nothing but toluene and a small amount of resinous material.

Experiment III.—

15.4 grams toluene.	N.D.$_{100}$ = 0.25 ampere.
210 cc. alcohol.	Voltage = 40–50.
15 grams sodium hydroxide.	Temperature, 20.5°.
30 cc. water.	Time, 10 hours.

There was no heat applied and the current produced no rise in temperature. The cup contents were acidified with hydrochloric acid and the sodium chloride which separated filtered off; subsequent distillation yielded only water, alcohol, and toluene, besides a small amount of brown resinous substance.

Experiment IV.—

63.7 grams toluene.	N.D.$_{100}$ = varying.
30 cc. acetone.	Voltage = varying.
Sodium hydrodixe to saturation.	Temperature, varying.
	Time, 2 hours.

On connecting the poles in circuit it was found that this solution would not conduct the current, so one cc. of a saturated solution of sodium hydroxide was added. The current was started at a normal density of 4.25 amperes and voltage of 13 ; after fifteen minutes the heat developed by the current was sufficient to make the acetone boil violently. The current was lowered to two and five-tenths amperes, the acetone still continuing to boil. In one hour and twenty minutes the temperature in the outer cup was 68°, and twenty minutes later one cc. of a saturated solution of sodium hydroxide was added. At the end of two hours the amperage had fallen to one and the voltage stood at seventy.

The anode liquid, on distilling off the acetone, yielded nothing but a small amount of tarry substance. This experiment showed that acetone would not serve as a solvent.

Experiment V.—

42.5 grams toluene.	N.D.$_{100}$ = 0.5 ampere.
20 grams sodium sulphate.	Voltage = 12-20.
100 cc. alcohol.	Temperature, 25°.
	Time, 9½ hours.

The alcohol and part of the toluene were removed by distillation and the anode liquid was then neutralized with barium carbonate. The neutral solution was shaken out with ether and this extract yielded, on fractionation, besides toluene, less than one cc. of a liquid of ester-like odor, which boiled between 39° and 44° under a pressure of twenty mm. The barium carbonate residue contained no organic products.

Experiment VI.—

42.5 grams toluene.	N.D.$_{100}$ = 0.5 ampere.
50 cc. alcohol.	Voltage = 80.
4 grams sodium sulphate.	Temperature, 75°.
	Time, 12 hours.

The current heat held the temperature at 75°. After twelve hours a strong-smelling layer of brown oily liquid separated on the top of the solution in the porous cup. This, on being neutralized with sodium carbonate and shaken out with ether, gave on fractionation a small amount of a liquid similar in odor to that obtained in the previous experiment, and which distilled under twenty mm. pressure almost constantly at 35°. Too small an amount of this was obtained to determine its composition. The residual liquid gave no organic products on being reacidified.

Experiment VII.—

42.5 grams toluene.	N.D.$_{100}$ = 1 ampere.
100 cc. alcohol.	Voltage = 40-50.
10 grams ammonium sulphate.	Temperature, 75°-80°.
	Time, 9½ hours.

During the electrolysis a very strong odor like that of impure acetamide was observed. After nine and one-half hours the current was interrupted and the upper oily layer which had separated, neutralized and dried over calcium chloride. On subjecting this liquid to fractionation, besides toluene and tarry matter, a very small amount of a sharp smelling substance was obtained, which distilled under seventy mm. pressure at 39°-42°.

It was then determined to increase the amperage, to see if a definite product could be obtained in some quantity.

Experiment VIII.—

42.5 grams toluene.	N.D.$_{100}$ = 1.5 amperes.
100 cc. alcohol.	Voltage = 11–14.
10 grams ammonium sulphate.	Temperature, 60°–65°.
	Time, 9½ hours.

As in the previous experiment, a strong odor like that of impure acetamide was observed. The anode liquid was neutralized by standing twelve hours over barium carbonate. On shaking out with ether and fractionating nothing but tarry products could be obtained. The residual liquid gave no organic products on being acidulated and shaken out with ether.

No further work was done in this direction, the oxidation of benzoin being taken up next.

Since a mixture of chromic and nitric acids readily oxidizes the methyl group in toluene to carboxyl, doubtless conditions can be found in which the same would be effected by electrolytic oxygen. The great obstacle in the above work was in obtaining a solvent that would give a solution of low resistance, and at the same time dissolve a sufficient amount of toluene. When such a solution is obtained the current density could certainly be found with which the desired oxidation would be accomplished.

ELECTROLYTIC OXIDATION OF BENZOIN.

The benzoin for the following experiments was prepared by treating 230 grams of benzaldehyde with 460 grams alcohol, 46 grams potassium cyanide, and 115 grams water. This solution was boiled under a return condenser on the water-bath for one hour. The crystals which separated on cooling were washed with cold alcohol, treated with bone-black in boiling alcohol, and the solution filtered and recrystallized. The crystals thus prepared melted at 134°.

In the work with benzoin both the oxidizing and reducing effects of the current were studied.

Oxidation of Benzoin in Alcoholic Sodium Hydroxide Solution.— The first experiment was made with an alkaline alcoholic solution of benzoin, the conditions being taken at random.
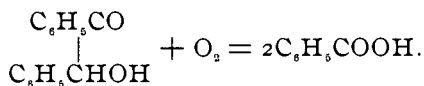
Experiment I.—

5 grams benzoin.	$N.D_{100} = 0.75$ ampere.
5 grams sodium hydroxide.	Voltage $= 3.8$
200 cc. alcohol.	Temperature. 60°.
	Time, 7 hours.

It was found necessary with the above proportions to heat the alcohol to 60° in order to keep the benzoin in solution; this was done by placing the beaker containing the porous cup on a water-ba''l. At the end of seven hours the anode liquid had an acid-reac..on. Hydrochloric acid was added to set free any organic acid that had been formed, and the liquid shaken out with ether. The ethereal extract, on evaporation, left a solid mass of an impure crystalline body. This was boiled up with barium carbonate and water, filtered, acidified, shaken out with ether, and the residue on sublimation gave crystals resembling benzoic acid, having a melting-point of 121.5°. An analysis of these crystals gave the following:

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Per cent. C calculated for C_6H_5COOH.
0.155	0.3875	68.11	68.85

	Weight of H_2O.	Per cent. H.	Per cent. H calculated for C_6H_5COOH.
	0.071	5.08	4.91

This identifies the body as benzoic acid, the oxidation proceeding according to the equation:

$$\begin{array}{l} C_6H_5CO \\ | \qquad\qquad + O_2 = 2C_6H_5COOH. \\ C_6H_5CHOH \end{array}$$

Besides the benzoic acid there was a large quantity of tarry decomposition product formed in this as well as in the following experiments.

The benzoic acid obtained was not weighed and the following experiments, II to VII inclusive, were made to find the conditions giving the best yield of benzoic acid.

The quantity of sodium hydroxide was increased because, as was noted above, the cup contents had an acid-reaction at the close of Experiment I.

Experiment II.—

5 grams benzoin.	N.D.$_{100}$ = 0.5 ampere.
10 grams sodium hydroxide.	Voltage = 4.5.
200 cc. alcohol.	Temperature, 60°.
	Time, 7 hours.

The anode liquid was still alkaline at the end of the time. The alcohol was evaporated, the residual liquid acidified with hydrochloric acid, shaken out with ether and the residue sublimed. A yield of sixteen per cent. of benzoic acid was obtained.

In the next experiment the amperage required by theory to convert all the benzoin to benzoic acid, was conducted through the solution.

Experiment III.—

5 grams benzoin.	N.D.$_{100}$ = 0.5 ampere.
10 grams sodium hydroxide.	Voltage = 3.8.
250 cc. alcohol.	Temperature, 60°.
	Time, 5 hours.

The anode liquid subjected to the same treatment as before gave 9.6 per cent. of benzoic acid.

In the next experiment the time was shortened and a marked decrease in yield noted.

Experiment IV.—

5 grams benzoin.	N.D.$_{100}$ = 0.5 ampere.
10 grams sodium hydroxide.	Voltage = 4.5.
250 cc. alcohol.	Temperature, 60°.
	Time, 3 hours.

The quantity of benzoic acid obtained was 8.2 per cent. In the next experiment the concentration was increased and the normal density lowered.

Experiment V.—

5 grams benzoin.	N.D.$_{100}$ = 0.25 ampere.
10 grams sodium hydroxide.	Voltage = 2.8.
150 cc. alcohol.	Temperature, 60°.
	Time, 7 hours.

These conditions gave eighteen per cent. of benzoic acid, the largest yield obtained by oxidation in alkaline solution.

In the following experiment the concentration and normal density were made the same as above and the time shortened.

Experiment VI.—

5 grams benzoin.	$N.D._{100} = 0.25$ ampere.
10 grams sodium hydroxide.	Voltage $= 2.8$
150 cc. alcohol.	Temperature, $60°$.
	Time, 5 hours.

The yield of benzoic acid in this case was 14.8 per cent.

To try the effect of higher amperage and longer time, both these factors were made twice as great as in Experiment V.

Experiment VII.—

5 grams benzoin.	$N.D._{100} = 0.5$ ampere.
10 grams sodium hydroxide.	Voltage $= 4$-5.
150 cc. alcohol.	Temperature, $60°$.
	Time, 14 hours.

The yield of benzoic acid obtained was 17.4 per cent. showing that no improvement was made by increasing time and normal density over that of Experiment V.

Oxidation of Benzoin in Alcoholic Sulphuric Acid Solution.

Experiment I.—

5 grams benzoin.	$N.D._{100} = 0.25$ ampere.
5 grams sulphuric acid (conc.).	Voltage $= 2.6$.
110 cc. alcohol.	Temperature, $60°$.
	Time, 7 hours.

On evaporating off about three-fourths of the alcohol from the anode liquid and cooling, crystallization set in. The crystalline mass was filtered off, washed with alcohol, redissolved in boiling alcohol and treated with bone-black ; when cool, white crystals separated which gave a melting-point of $134°$, proving the substance to be unchanged benzoin.

The concentration, time, and normal density were increased in the next experiment in order to effect the oxidation.

Experiment II.—

5 grams benzoin.	$N.D._{100} = 0.5$ ampere.
5 grams sulphuric acid (conc.).	Voltage $= 3.8$.
100 cc. alcohol.	Temperature, $60°$.
	Time, 10 hours.

The anode liquid was neutralized with sodium carbonate, after having the greater part of the alcohol removed by evaporation; a layer separated at this point having the odor of ethyl benzoate.

This ester layer was separated, and distilled between 200° and 215°; its saponification yielded benzoic acid. The lower layer after the removal of the ester was extracted with ether, the solvent evaporated, and the residue sublimed. This gave one and a half per cent. of benzoic acid, while the ester above held 15.8 per cent. in combination, making a total yield of 17.3 per cent.

The analysis of this acid gave the following:

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Per cent. of C calculated for C_6H_5COOH.
0.3960	0.9975	68.69	68.85

	Weight of H_2O.	Per cent. of H.	Per cent. of H calculated for C_6H_5COOH.
	0.181	5.07	4.91

The residue from the ether extract above was of a yellow color, which could be removed by chloroform, but on evaporation only a tarry mass was left.

The effect of an increase in normal density was tried in the next experiment, the other factors remaining the same.

Experiment III.—

5 grams benzoin.	$N.D._{100} = 1.5$ amperes.
5 grams sulphuric acid (conc.).	Voltage = 9–10.
100 cc. alcohol.	Temperature, 60°.
	Time, 10 hours.

The anode liquid, worked up as before, gave for the total of free benzoic acid and that combined as ethyl benzoate only two and eight-tenths per cent. The quantity of tarry matter present was larger than in any previous experiment of this series.

Oxidation of Benzoin in Alcoholic Hydrochloric Acid Solution.— For the following experiments an anode of carbon was used together with a porous cup similar to that of the previous line of experiments. The outer liquid was a twenty per cent. hydrochloric acid solution. As benzoic acid resulted from the above oxidations, it was believed that it might be possible to prepare a chlorinated benzoic acid by working with a hydrochloric acid solution. The reaction, however, took a different course as the following experiments show:

Experiment I.—

5 grams benzoin.	$N.D._{100} = 1$ ampere.
20 cc. hydrochloric acid (conc.).	Voltage = 2.3.
100 cc. alcohol.	Temperature, 60°.
	Time, 9 hours.

On account of the size of the carbon electrode the anode chamber was left open and the alcohol, that escaped by evaporation, replaced from time to time.

When the cup contents cooled, a mass of ill-defined crystals separated. The supernatant liquid was decanted, the mass washed with cold alcohol and dried. The substance was then sublimed, giving crystals resembling benzoic acid; these were subjected to two more sublimations, then dissolved in sodium carbonate, and reprecipitated; a final sublimation yielded crystals which melted at 121°. A yield of three and two-tenths per cent. of benzoic acid was obtained.

A small amount of a yellow solid separated from the supernatant liquid on the removal of the alcohol. This same yellow body separated from the benzoic acid at the point in its purification where it was treated with sodium carbonate solution. The two portions were combined, dissolved in alcohol, treated with bone-black, filtered, and recrystallized, giving a melting-point of 94°. Not enough of this body was obtained at this point for analysis, but as will be seen in the succeeding experiments, it proved to be benzil, and changes in the working conditions produced it with no accompanying yield of benzoic acid.

The analysis of the above acid gave the following:

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Per cent. C calculated for C_6H_5COOH.
0.165	0.420	69.83	68.85

	Weight of H_2O.	Per cent. H.	Per cent. H calculated for C_6H_5COOH.
	0.0825	5.58	4.91

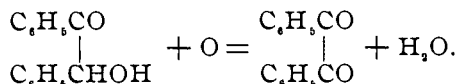*Experiment II.—*

5 grams benzoin. $N.D._{100} = 2$ amperes.
25 cc. hydrochloric acid (conc.).   Voltage $= 3$.
150 cc. alcohol.   Temperature, 60°.
                 Time, 12 hours.

When the cup contents cooled some benzoin crystallized out. The liquid had a strong odor of ethyl acetate. On evaporating off the alcohol and ethyl acetate an oily substance separated, which solidified when the residual liquid cooled; this was removed, dissolved in alcohol, treated with bone-black, and allowed to crystallize; the body thus obtained gave a melting-point of 94°. The analysis of this body gave the following:

Weight of substance in gram.	Weight of CO_2.	Per cent. of C.	Per cent. of C calculated for $C_{14}H_{10}O_2$.
0.161	0.463	79.04	80.00

	Weight of H_2O.	Per cent. of H.	Per cent. of H calculated for $C_{14}H_{10}O_2$.
	0.0655	4.52	4.76

This analysis, together with the properties of the body, identify it as benzil, $C_{14}H_{10}O_2$. The oxidation in hydrochloric acid solution then proceeds according to the equation:

$$\begin{array}{c} C_6H_5CO \\ | \\ C_6H_5CHOH \end{array} + O = \begin{array}{c} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + H_2O.$$

No benzoic acid could be found among the products of the oxidation.

Experiment III.—

    5 grams benzoin.   N.D.$_{100}$ = 3 amperes.
    60 cc. hydrochloric acid (conc.).   Voltage = 2.7.
    140 cc. alcohol.   Temperature, 70°–75°.
                              Time, 10 hours.

The anode liquid worked up as in the preceding experiment gave seven and five-tenths per cent. of benzil, and a careful examination failed to show any benzoic acid.

In the next experiment the quantity of hydrochloric acid was decreased and the temperature raised to 75°–80°.

Experiment IV.—

    5 grams benzoin.   N.D.$_{100}$ = 3 amperes.
    25 cc. hydrochloric acid (conc.).   Voltage = 2.8–3.
    150 cc. alcohol   Temperature, 75°–80°.
                              Time, 10 hours.

The porous cup was connected with an inverted condenser, yet at this temperature some of the alcohol escaped through the part of the cup above the line of the liquid, necessitating additions from time to time.

When the cup contents cooled, benzoin to the amount of thirty-one per cent. crystallized out. The yield of benzil in this experiment, based on the amount of benzoin decomposed, was 28.3 per cent.

The effect of increased normal density was tried in the following experiment:

Experiment V.—

5 grams benzoin.	$N.D._{100} = 6$ amperes.
25 cc. hydrochloric acid (conc.).	Voltage $= 4.3$.
150 cc. alcohol.	Temperature, $75°-80°$.
	Time, 10 hours.

As in Experiment IV considerable benzoin separated from the anode liquid on cooling. The yield of benzil here, based on the amount of benzoin decomposed, was sixty-two per cent.

The effect of a still greater normal density, together with an increase in the amount of hydrochloric acid, was tried in the next experiment.

Experiment VI.—

2.5 grams benzoin.	$N.D_{100} = 8$ amperes.
50 cc. hydrochloric acid (conc.).	Voltage $= 4.6$.
125 cc. alcohol.	Temperature, $68°$.
	Time, 10 hours.

No heat was applied to the solution, that developed by the current holding the temperature nearly constant at $68°$. No benzoin remained over in this experiment and the yield of benzil was 75.4 per cent.

Since in none of the above experiments was there any chlorinated product, the following conditions were tried to prepare such a body:

Experiment VII.—

2.5 grams benzoin.	$N.D_{100} = 6$ amperes.
100 cc. hydrochloric acid (conc.).	Voltage $= 5-6$.
100 cc. alcohol.	Temperature, $65°-70°$.
	Time, 19 hours.

A dark brown pasty mass separated on cooling the anode liquid. The residual liquid after evaporation of the alcohol, deposited more of a similar material. Sublimation was tried with some of this tarry product, but no well-defined body could be obtained. Various attempts to isolate a definite product from this pasty mass resulted in failure.

ELECTROLYTIC REDUCTION OF BENZOIN.

With the exception of a small quantity of a substance melting at $205°-206°$, obtained both in hydrochloric and sulphuric acid solutions, the following experiments led to no definite results.

Reduction of Benzoin in Alcoholic Sodium Hydroxide Solution.

Experiment I.—

5 grams benzoin.	$N.D._{,100} = 0.5$ ampere.
5 grams sodium hydroxide.	Voltage $= 3.6$.
150 cc. alcohol.	Temperature, $60°$.
	Time, 10 hours.

The cathode liquid was neutralized with hydrochloric acid, the alcohol removed by evaporation, some water added, and the whole shaken out with ether. The ethereal extract yielded a very small quantity of a white crystalline substance, which on purification melted with decomposition at $204°–210°$.

Experiment II.—

5 grams benzoin.	$N.D._{,100} = 4$ amperes.
5 grams sodium hydroxide.	Voltage $= 6–7$.
200 cc. alcohol.	Temperature, $70°–75°$.
	Time, 15 hours.

The above temperature was produced by the heating effect of the current alone. The cathode liquid was neutralized with hydrochloric acid, and the alcohol removed. From the residual liquid, on cooling, a yellow pasty substance separated together with a mass of white needle-like crystals resembling benzoic acid. The latter were separated, and purified by dissolving in sodium carbonate solution, reprecipitated by hydrochloric acid and sublimed; the product gave a melting-point of $121°$, and agreed with benzoic acid in all its properties. The yield of benzoic acid was 4.9 per cent.

The yellow pasty substance resisted all attempts at crystallization, though all the solvents at hand were tried.

Experiment III.—

2.5 grams benzoin.	$N.D._{,100} = 4$ amperes.
5 grams sodium hydroxide.	Voltage $= 7$
100 cc. alcohol.	Temperature, $70°–78°$.
25 cc. water.	Time, 10 hours.

The current heat in this experiment kept the temperature between $70°$ and $78°$. A new porous cup was used and much trouble was caused by the accumulation of silicic acid between the anode and the cup. The current was stopped every two hours in order that this gelatinous mass might be removed.

The cathode liquid on standing over night separated into two layers; the whole was neutralized with hydrochloric acid and the alcohol evaporated. The residual liquid, on cooling, deposited a dark pasty mass, which on being removed dissolved in alcohol, imparting a purple color to the solution. It was found on evaporating this solution to crystallization, that a white flocculent mass separated, portions of which, exposed to the air, oxidized to a purple color like that of the alcoholic solution. Not enough of this material could be obtained in a pure state for analysis. The purple alcoholic liquid on complete evaporation left a blue mass which on sublimation gave benzoic acid.

Experiment IV.—

2.5 grams benzoin.	$N.D_{100} = 4$ amperes.
5 grams sodium hydroxide.	Voltage = 4.
100 cc. alcohol.	Temperature, $50°-55°$.
	Time. 9 hours.

The heat of the current kept the temperature between 50° and 55°.

Nothing separated from the cathode liquid on standing, but when neutralized with hydrochloric acid a flocculent precipitate separated; this was filtered off, washed with water to free it from sodium chloride, and dissolved in alcohol ; several attempts were made to crystallize it, but this could not be effected. No well-defined body could be isolated from the filtrate above after the removal of the alcohol.

The formation of benzoic acid in Experiments II and III probably resulted from air oxidation of the unstable reduction products after their removal from the porous cup.

Reduction of Benzoin in Alcoholic Sulphuric Acid Solution.

Experiment I.—

5 grams benzoin.	$N.D._{100} = 1.5$ amperes.
5 grams sulphuric acid (conc.).	Voltage = 3.6.
100 cc. alcohol.	Temperature, $70°$.
	Time, 10 hours.

The cathode liquid was shaken out with ether, and this extract crystallized from alcohol after treatment with bone-black. After a second crystallization the body melted with decomposition at 235°. Not enough of this substance was obtained for analysis.

In the next experiment the temperature was increased.

Experiment II.—

5 grams benzoin.	N.D.$_{100}$ = 1.5 amperes.
5 grams sulphuric acid (conc.).	Voltage = 4.6.
100 cc. alcohol.	Temperature, 75°–78°.
	Time, 10 hours.

A crystalline mass lined the sides of the vessel when the cathode liquid had cooled. A purification of this material yielded a very small amount of a white substance, consisting of minute crystals which melted between 205° and 206°. Such a small quantity of this body was obtained that the analytical results can have but little value. The figures obtained are as follows:

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Weight of H_4O.	Per cent. H.
0.0605	0.1945	87.66	0.0345	6.33

The simplest formula for this body would then be $C_{22}H_{19}O$.

In the third experiment of this series, the normal density was increased and also the quantity of sulphuric acid.

Experiment III.—

5 grams benzoin,	N.D.$_{100}$ = 4.5 amperes.
20 grams sulphuric acid (conc.).	Voltage = 6.5.
100 cc. alcohol.	Temperature, 75°.
	Time, 10 hours.

The current heat was sufficient to keep up the temperature. At the end of the time, adhering to the cathode and cell wall, was a yellow pasty mass which was detached, and on purification gave crystals similar in appearance to those obtained in Experiment II, and having the same melting-point, 205°–206°. The alcoholic filtrate yielded a small additional amount of the same body. As before the quantity of pure substance obtained was too small for a reliable analysis. The combustion gave the following:

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Weight of H_2O.	Per cent. H.
0.034	0.161	88.63	0.014	4.57

These results approximate the formula $C_{22}H_{14}O$.

Reduction of Benzoin in Alcoholic Hydrochloric Acid Solution.

Experiment I.—

2.5 grams benzoin. $N.D._{\cdot 100} = 4.5$ amperes.
25 cc. hydrochloric acid (conc.).   Voltage = 7.
75 cc. alcohol.   Temperature, 75°.
                                      Time, 10 hours.

An anode of carbon was used in this as in the other experiments of this series. The current heat was sufficient to keep up the temperature.

When the cathode liquid cooled, a small amount of a yellow material deposited, which on purification by bone-black and boiling alcohol gave a white crystalline body having a melting-point of 205°–206°. The mother-liquor from these crystals, and that decanted from the cup in the first place, when combined and concentrated, gave a yellow paste which could not be crystallized, though portions of it were tried with the various solvents.

The quantity of pure material above, which melted at 205°–206°, was too small to make a trustworthy analysis. The combustion gave the following :

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Weight of H_2O.	Per cent. H.
0.0458	0.1451	86.39	0.023	5.58

This analysis approximates the formula $C_{14}H_{11}O$.

ELECTROLYTIC OXIDATION OF BENZIL.

The benzil used in the following experiments was prepared according to the method given in Gattermann's "Practical Methods of Organic Chemistry." Crude benzoin was finely pulverized and heated in an open flask with frequent shaking, with twice its weight of pure concentrated nitric acid, for two hours on a rapidly boiling water-bath. When the oxidation was ended the reaction mixture was poured into cold water; after the mass solidified the nitric acid was poured off; it was then washed several times with cold water, pressed out on a porous plate and crystallized from alcohol. After filtering off the separated crystals, they were dried in the air on several layers of filter-paper. The crystals melted at 94°.

The experiments in this series were carried out in a manner nearly analogous to those with benzoin.

Oxidation of Benzil in Alcoholic Sodium Hydroxide Solution.

Experiment I.—

2.5 grams benzil.	N.D.$_{100}$ = 0.5 ampere.
5 grams sodium hydroxide.	Voltage = 9.
100 cc. alcohol.	Temperature, 40°–50°.
	Time, 10 hours.

The heat developed by the current was sufficient to hold the temperature between the above limits.

After neutralization of the alkali, evaporation of the alcohol and extraction with ether, nothing but a tarry mass was obtained, from which nothing definite could be isolated.

Experiment II.—

2.5 grams benzil.	N.D.$_{100}$ = 1 ampere.
5 grams sodium hydroxide.	Voltage = 9–45.
100 cc. alcohol.	Temperature, 70°.
	Time, 6 hours.

The current kept the solution heated to 70°. The resistance of the solution increased so that at the end of six hours the current was stopped, the voltage having risen to forty-five.

The solution, treated as in Experiment I, yielded nothing but tarry products.

Experiment III.—

2.5 grams benzil.	N.D.$_{100}$ = 0.5 ampere.
5 grams sodium hydroxide.	Voltage = 2.2.
75 cc. alcohol.	Temperature, 40°.
	Time, 6 hours.

A muslin bag was used instead of the porous cup for this experiment and a marked lowering of the resistance effected. The current heat alone raised the temperature to 40°.

The anode liquid yielded nothing but undecomposed benzil and tarry decomposition products as before.

*Oxidation of Benzil in Alcoholic Sulphuric Acid Solution.*

Experiment I.—

2.5 grams benzil.	N.D.$_{100}$ = 3 amperes.
20 grams sulphuric acid (conc.).	Voltage = 6.5°.
100 cc. alcohol.	Temperature, 65°.
	Time, 10 hours.

The above temperature was maintained by the current heat alone.

When the alcohol was evaporated from the dark-colored anode liquid the odor of ethyl benzoate was observed. The ester was not separated, but the whole was shaken out with benzene and ligroin, the solvent removed and the residual liquid treated with an excess of sodium hydroxide and subjected to the heat of the water-bath for several hours. After the saponification of the ester, the liquid was acidified, shaken out with a mixture of ether and benzene and the solvent evaporated; the sublimation of the residue yielded crystals resembling benzoic acid, having a melting-point of 121°. A yield of eight and seven-tenths per cent. was obtained and the analysis gave the following:

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Per cent. C calculated for C_6H_5COOH.
0.2442	0.6162	68.81	68.85

	Weight of H_2O.	Per cent. H.	Per cent. H calculated for C_6H_5COOH.
	0.1041	4.70	4.91

The reaction then proceeded according to the equation

$$\begin{array}{c} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + H_2O + O = 2C_6H_5COOH.$$
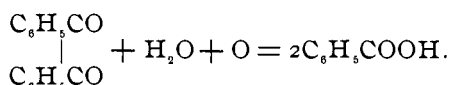
Experiment II.—

2.5 grams benzil	$N.D._{100} = 1$ ampere.
20 grams sulphuric acid (conc.).	Voltage = 10.5.
100 cc. alcohol.	Temperature, 65°.
	Time, 10 hours.

No outside heat was applied, the current alone raising the temperature to 65° at the end of one and one-half hours.

On subjecting the anode liquid to the same treatment as in Experiment I, a yield of 14.5 per cent. benzoic acid was obtained.

Oxidation of Benzil in Alcoholic Hydrochloric Acid Solution.

Experiment I.—

5 grams benzil.	$N.D._{100} = 1$ ampere.
20 cc. hydrochloric acid (conc.).	Voltage = 3.
75 cc. alcohol.	Temperature, 60°.
	Time, 10 hours.

Nothing but benzil separated when the cup contents cooled, and the alcoholic filtrate contained benzil and a small amount of tarry substance.

For the next experiment the normal density was increased to seven amperes.

Experiment II.—

5 grams benzil	N.D.$_{100}$ = 7 amperes.
25 cc. hydrochloric acid (conc.).	Voltage = 6.
100 cc. alcohol.	Temperature, 70°–75°.
	Time, 9 hours.

Here again a crystalline mass of benzil separated when the anode liquid cooled. The alcoholic filtrate contained nothing but benzil and some tarry decomposition products.

ELECTROLYTIC REDUCTION OF BENZIL.

Reduction in Alcoholic Sodium Hydroxide Solution.

Experiment I.—

2.5 grams benzil.	N.D.$_{100}$ = 0.5 ampere.
5 grams sodium hydroxide.	Voltage = 3.3.
100 cc. alcohol.	Temperature, 30°.
	Time, 6 hours.

A muslin bag was used for the porous septum in this experiment. The current kept the temperature at 30°.

The cathode liquor was neutralized with hydrochloric acid and the alcohol removed by evaporation. The residual liquid on cooling deposited a small amount of a white crystalline material, together with the unchanged benzil, which collected in a lump. The white crystals were readily soluble in cold alcohol and to a less degree in hot water. After a crystallization from hot water the crystals melted with some decomposition at 145°–146°. Not a sufficient quantity of this body was obtained for a combustion.

Experiment II.—

2.5 grams benzil.	N.D.$_{100}$ = 3 amperes.
5 grams sodium hydroxide.	Voltage = 5.
100 cc. alcohol.	Temperature, 50°.
	Time, 6½ hours.

The current heat held the temperature at 50°. After neutralization with hydrochloric acid and removal of the alcohol, a small amount of white needle-like crystals separated, together with benzil and some tarry matter. The crystals were separated, dissolved in hot water, treated with bone-black, and recrystallized.

The body had no definite melting-point, beginning to fuse and decompose at 185°.

Reduction of Benzil in Alcoholic Sulphuric Acid Solution.

Experiment I.—

2.5 grams benzil.	N.D.$_{.100}$ = 4 amperes.
20 grams sulphuric acid (conc.).	Voltage = 9.
100 cc. alcohol.	Temperature, 65°.
	Time, 15½ hours.

No outside heat was applied, the current holding the temperature at 65°. On standing over night a small amount of a white crystalline substance separated, which was removed and purified, giving a melting-point of 205°–206°. The removal of the alcohol caused the deposition in small amount of a yellow, pasty mass, which oxidized very readily and could not be crystallized.

The white crystalline body above is probably the same as that obtained in several previous reductions. So little of these substances melting at 205°–206° was obtained in the various reductions that the analytical results have little value in establishing their identity, although the physical properties are the same. The white body obtained in this reduction analyzed as follows, approximating the formula $C_{38}H_{24}O$:

Weight of substance in gram.	Weight CO_2.	Per cent. C.	Weight H_2O.	Per cent. H.
0.048	0.161	91.46	0.0215	4.97

Experiment II.—

2.5 grams benzil.	N.D.$_{.100}$ = 1 ampere.
20 grams sulphuric acid (conc.).	Voltage = 4.
100 cc. alcohol.	Temperature, 40°.
	Time, 10½ hours.

The current heat alone kept up the temperature. When the current was interrupted it was found that a mass of white crystals lined the walls of the porous cup and adhered to the cathode. The crystals were washed with water, dissolved in alcohol, treated with bone-black and crystallized, melting sharply at 134°. When sublimed, these crystals suffered decomposition. In physical properties the body resembled benzoin and the analysis confirms this:

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Per cent. C calculated for benzoin $C_{14}H_{12}O_2$.
0.189	0.5495	79.28	79.24

Weight of H_2O.	Per cent. H.	Per cent. H calculated for benzoin $C_{14}H_{12}O_2$.
0.0985	5.78	5.66

The reaction then proceeds according to the equation:

$$\begin{array}{ccc} C_6H_5CO & & C_6H_5CO \\ | & + H = & | \\ C_6H_5CO & & C_6H_5CHOH \end{array}$$
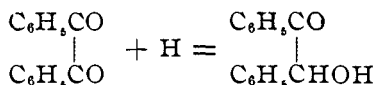
The yield of benzoin obtained was 31 per cent.

Reduction of Benzil in Alcoholic Hydrochloric Acid Solution.

Experiment I.—

5 grams benzil.	$N.D._{.100} = 1$ ampere.
20 cc. hydrochloric acid (conc.).	Voltage = 2.2.
150 cc. alcohol.	Temperature, $30°$.
	Time, 10 hours.

No external heat was applied. As with the sulphuric acid solution, there were white crystals hanging in masses to the cathode and the walls of the porous cup. These crystals were purified as in the above experiment and melted sharply at $134°$. The alcoholic filtrate yielded more of the benzoin, making a total yield of 39 per cent. The analysis gave the following:

Weight of substance in gram.	Weight of CO_2.	Per cent. C.	Per cent. C calculated for benzoin $C_{14}H_{12}O_2$.
0.206	0.6075	80.42	79.24

	Weight of H_2O.	Per cent. H.	Per cent. H calculated for benzoin $C_{14}H_{12}O_2$.
	0.105	5.66	5.66

SUMMARY.

Comparison of the Above Results with those Obtained by the Usual Oxidizing and Reducing Agents.

Benzoin, when treated with chromic acid, yields benzaldehyde and benzoic acid, while Fehling's solution, nitric acid, or chlorine oxidizes it to benzil.

The electrolytic oxidation in sodium hydroxide solution with normal density of 0.25 ampere gave the maximum yield of benzoic acid, while higher densities gave less acid and larger quantities of tarry decomposition products. With sulphuric acid solution the normal density had to be raised five-tenths ampere in order to effect oxidation, yet an increase in density here, as with the sodium hydroxide solution, gave more tarry matter and less benzoic acid.

In hydrochloric acid solution the experiment with normal density at one ampere gave as oxidation products both benzoic acid and benzil, while densities above this gave large yields of benzil alone, and an increase in both time and density factors gave only tarry decomposition products.

Sodium amalgam or benzoin yields hydrobenzoin together with a little isohydrobenzoin. Zinc and hydrochloric acid reduction of benzoin yields desoxybenzoin.

The experiments on the electrolytic reduction of benzoin gave as the only definite product the body melting at 205°–206°, which was obtained both in hydrochloric and sulphuric acid solutions.

The ordinary chromic acid oxidation of benzil yields benzoic acid.

With sodium hydroxide solution and densities of five-tenths and one ampere the electrolytic oxidation of benzil gave no definite products even when, as in one case, some benzil remained in the cup unchanged.

In sulphuric acid solution the electrolytic oxidation of benzil gave benzoic acid, 14.5 per cent. being the highest amount obtained.

With electrolytic oxygen in hydrochloric acid solution, benzil was unchanged when the normal density was equal to one ampere and an increase to seven amperes gave only a partial decomposition and indefinite tarry substances.

Benzil reduced by zinc and hydrochloric acid gives benzoin or desoxybenzoin according to the conditions.

The electrolytic reduction of benzil in sodium hydroxide solution gave nothing definite.

In sulphuric acid solution, benzil gave by the current reduction benzoin, the product crystallizing in an almost pure condition on the walls of the porous cup. An increase in the time factor gave besides decomposition products, a small amount of the body melting at 205°–206°, which is evidently the same as that obtained in the reduction of benzoin in both sulphuric and hydrochloric acid solutions.

By the current reduction in hydrochloric acid solution benzil gave benzoin in a crystalline form that was almost pure when taken from the cup.