# THE ELECTROLYTIC REDUCTION OF SUBSTITUTED BENZOIC ACIDS

## I. HALOBENZOIC ACIDS

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## I. HALOBENZOIC ACIDS

By

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# ABSTRACT

The purpose of this investigation was as follows: To determine the optimum conditions for the electrolytic reduction of ortho-bromobenzoic acid and to test the suitability of these conditions for the preparation of other substituted benzyl alcohols.

Forty-nine experiments were carried out in the following manner: The electrolytic cell was assembled, the acid to be reduced was placed in the catholyte and a current passed for a specified period of time. At the end of the experiment the benzyl alcohol was separated from any unreacted benzoic acid and the two compounds purified by conventional methods. The detailed conditions used and the results obtained in these experiments are listed in tabular form in this thesis.

The most suitable conditions for the reduction appear to be a lead dioxide cathode, an alcohol-sulfuric acid catholyte and a high current density. The porous cups (which contain the anolyte) should be thoroughly cleaned before use in order to remove any iron salts present as impurities.

Electrolytic reduction of the corresponding acid was found to be a desirable method of preparation for the mono chloro- and bromo-benzyl alcohols. This method of reduction appears to be of limited application for the

preparation of iodo- and dichloro-benzyl alcohols because of the relative insolubility of the corresponding acids in an alcohol-sulfuric acid catholyte. In general, the more soluble the substituted benzoic acid, the better the yield of the corresponding benzyl alcohol and the greater the current efficiency.

Para-bromo-, para-iodo-, and 2,6-dichloro-benzyl alcohols have been prepared for the first time by electrolytic reduction of the corresponding acids. The latter alcohol (2,6-dichlorobenzyl) is previously unreported in the literature.

# ACKNOWLEDGEMENT

The author wishes to express his deep appreciation for the help and encouragement of Professor Ralph L. Guile during the course of this investigation.

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# INTRODUCTION

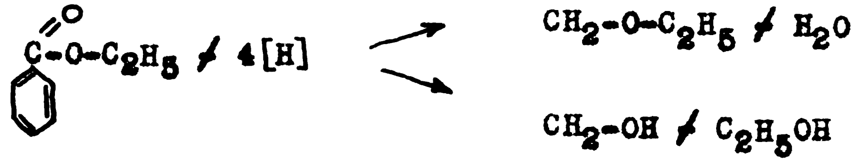
Halogen substituted benzyl alcohols are not available commercially, and the synthesis of some of these alcohols, for example the ortho bromo isomer, by the usual organic chemical methods is not too satisfactory. Since many halogen substituted aromatic acids are either commercially available or easily synthesized from available substances, electrolytic reduction of such benzoic acids would be a convenient method for the synthesis of halobenzyl alcohols.

Fichter (1) lists many examples of aromatic acids which have been successfully reduced to the corresponding alcohols in excellent yields. Many of these reductions were carried out by Mettler (2) (3) (4), but attempts by Wu (5) in this laboratory to prepare o-bromobenzyl alcohol by the method of Mettler were not too successful.

The purpose of this investigation was as follows: Mettler's work with o-bromobenzoic acid was to be repeated, different conditions leading to variations in yields of the o-bromobenzyl alcohol were to be investigated, and finally other alcohols were to be prepared using the technique developed for the preparation of the o-bromobenzyl alcohol.

# HISTORICAL BACKGROUND

The first electrolytic preparation of benzyl alcohol was accomplished, not by the reduction of benzoic acid, but by the reduction of esters of benzoic acid. In 1904-1905 Mettler reported (6) (7) that by using a lead cathode and an alcoholic sulfuric acid catholyte ethyl benzoate could be electrolytically reduced to benzyl alcohol.



However along with the alcohol benzyl ethyl ether was also formed. Mettler obtained similar results with methyl benzoate as well as with esters of o-chloro-m-chloro-, and m-bromobenzoic acids. Since the yields of the ethers were higher than the yields of the alcohols this was not a very satisfactory method for the preparation of benzyl alcohols.

Tafel and Friedrichs (8) also reported that the ethyl and methyl esters of benzoic acid may be reduced to the corresponding benzyl ethers, but they did not mention the production of any benzyl alcohol. They used a lead cathode at a temperature of 12°C. and a current density of 10 amps. per sq. dm.

Mettler (3) (4) was the first investigator to successfully reduce aromatic acids to the corresponding alcohols. By working with a lead cathode and an alcoholic sulfuric acid catholyte he was able to bring about the reduction of numerous aromatic acids.

$$Ar\text{-}COOH + 4[H] \longrightarrow Ar\text{-}CH_2OH + H_2O$$

Some of the acids he reduced were benzoic acid, the three mono-chlorobenzoic acids, and m-bromobenzoic acid. Mettler reported that the concentration of sulfuric acid had no influence upon the chemical yield of the alcohol or the current efficiency.

The process was carried out at room temperature by cooling with a water bath, because there was danger of esterification at higher temperatures. A cathode area of 1 sq. dm. and a current density of 6-12 amps./sq. dm. were used. The catholyte was composed of 30 grams of sulfuric acid, 70 grams of alcohol, and 20 grams of the acid to be reduced. It was possible to replace some alcohol with water in order to increase the conductivity of the catholyte. Mettler found that, in the reduction of benzoic acid, it was possible to substitute water for one half of the alcohol in the catholyte, use a temperature of 50-60°C., and add the benzoic acid portionwise.

Mettler was unable to reduce benzoic acid suspended in cold aqueous sulfuric acid of various concentrations.

In the reduction of these aromatic acids Mettler used what is known as a "prepared" lead cathode. This type of electrode is made by Tafel's method, i.e., electrolytic oxidation of the lead in a 20% sulfuric acid solution (9). According to Tafel (10) the surface film of lead dioxide which is formed has a higher overvoltage and is more active than a plain lead cathode.

Both Mettler (2) and Tafel (9) found that the porous cups used in electrolytic organic reductions had to be cleaned with NaOH and HCl in order to remove iron salts which were present as impurities.

Mettler later reported (6) the reduction of more aromatic acids by the same method. In this article he mentioned that o-bromobenzoic acid can be successfully reduced to o-bromobenzyl alcohol, and although no yields of specific alcohols were given, he stated that in general yields of 60-85% may be expected. In the reduction of m-iodobenzoic acid, benzyl alcohol is formed along with the expected m-iodobenzyl alcohol, and with o-iodobenzoic acid only benzyl alcohol is formed.

Much of the later work on electroytic reduction of aromatic acids was carried out with benzoic acid. Inoue (11) repeated Mettler's work with benzoic acid and obtained a 78% yield of benzyl alcohol.

Lecans and Dufour (12) carried out the reduction of benzoic acid with a lead cathode, but in contrast to Mettler they used boiling aqueous sulfuric acid (60%) as the catholyte, and added the benzoic acid a little at a time (this minimized esterfication). They found a cathode density of 12-13 amps./sq. dm. to be optimum current density. Besides the benzyl alcohol (75-80%), some dibenzyl ether $(C_6H_5\text{-}CH_2)_2O$ (16-20%), iso-hydrobenzoin $C_6H_5\text{-}CH(OH)\text{-}CH(OH)\text{-}C_6H_5$ (1-2%), and tar (3%) were obtained. Although benzaldehyde was not detected they believed that the production of isohydrobenzoin was evidence of benzaldehyde as an intermediate in the reduction.

Baur and Muller (13) carried out the reduction of benzoic acid using a lead cathode, a dilute alcoholic sulfuric acid catholyte, and a low current density (2 amps./sq. dm.). In addition to benzyl alcohol they obtained a product with the empirical formula $C_6H_8O$ which they claimed was $\Delta^2$-cyclohexenone. However Somlo (14) pointed out that this compound had the properties of the ethyl ester of $\Delta^{1,3}$-dihydrobenzoic acid which would be formed by hydrogenation of the ring.

Fichter and Stein (15) also repeated Mettler's work and obtained an 80% yield of benzyl alcohol. They believed that hydrogenation of the ring as observed by Baur and Muller was due to the very low current density that the latter used.

Swann and Lucker (16) studied the reduction of benzoic acid by the Mettler method at cathodes of cadmium, tin, lead, mercury, zinc, aluminum, nickel, copper and iron. They reported that good yields of benzyl alcohol were obtained only with lead and cadmium electrodes. According to them the physical structure of the cathode surface was an important factor in controlling the yield.

They also found that a lead cathode will lose its activity after prolonged use. This loss of activity was accompanied by excessive formation of lead sulfate on the surface and several days of "preparation" by the Tafel method would not bring about a resumption in activity of the lead cathode. When using cadmium cathodes they found that the yield of alcohol was dependent upon the ability of the cathode to undergo a macro-etch of its surface, and that the yield of alcohol was proportional to the extent of such etching. Little or no yield resulted when the surface would not undergo an etch. Yields at other common metal electrodes were not improved by etching the surfaces.

Nithack (17) was able to reduce benzoic acid to bensaldehyde by the use of graphite electrodes and 20% sulfuric acid.

Other investigators have found that the reduction of salicylic acid at mercury electrodes in boric acid solution can be stopped at the aldehyde stage if some method of removing thesalicylaldehyde is used. Weil (18) used para-toluidine to form a Schiff's base with the salicylaldehyde and prevent further reduction. Mettler (19) found that, if benzene were added to the catholyte and the system stirred vigorously, the aldehyde would dissolve in the benzene phase and be protected from further electrolytic action. The best results were obtained by Tesh and Lowy (20) who fixed the aldehyde as soon as formed by means of sodium bisulfite and then recovered the salicylaldehyde by means of acid hydrolysis and distillation. Their best yield was 55%.

Rutovskii and Korolev (21) repeated Tesh and Lowy's work but obtained yields of only 34%. They also found that o-hydroxybenzyl alcohol was the main product when benzene and magnesium butyrate were used in the catholyte.

In acid solution at lead electrodes Mettler (19) and Somlo (22) reported that the expected o-hydroxybenzyl alcohol was formed.

Electrolytic reduction of o-bromobenzoic acid by Wu (5) in this laboratory was not too satisfactory. Five experiments resulted in yields of 40%, 30%, 15%, 0%, and 0% o-bromobenzyl alcohol. The conditions used were similar to those described by Mettler (2) (3) except that a current density of 5-6 amps./sq. dm., and a plain lead cathode were used.

Olivier (23) attempted to prepare 2,6-dibromobenzyl alcohol from 2,6-dibromobenzoic acid by the Mettler method. However he found that one bromine atom was eliminated as hydrogen bromide and o-bromobenzyl alcohol was formed. He stated that the second bromine in position 6 increases the mobility of bromine in position 2.

On the other hand Mettler (2) has successfully reduced 3,5-dibromosalicylic acid to 3,5-dibromosalicyl alcohol. He has also (2) reduced 3,5-dichlorosalicylic acid and 3,5-dichloro-4-hydroxybenzoic acid to the corresponding alcohols.

A number of other investigators have successfully used the method of Mettler for the reduction of aromatic acids. Olivier (24) has prepared p-tolyl carbinol from p-toluic acid; Mayer and English (25) have reduced 2-ethylbenzoic acid to the corresponding alcohol, and Mayer, Schafer, and Rosenbach (26) have reduced a series of substituted anthranilic acids. Detailed instructions for the reduction of anthranilic acid are given by Coleman and Johnson (27) in "Organic Syntheses". They used essentially the same conditions as Mettler, the catholyte being aqueous sulfuric acid since anthranilic acid is fairly soluble in aqueous sulfuric acid.

Side chain acids have been successfully reduced at a lead cathode in sulfuric acid solution. Kling (28) (29) reports the reduction of ortho, meta, and para tolylacetic acids to the corresponding ethyl alcohols using these conditions. Marie and Marquis (30) were able to obtain beta-phenylethyl alcohol by the reduction of phenyl acetic acid at lead electrodes. However they found that electrolysis at 60°C., using an alcoholic sulfuric acid catholyte, resulted in the formation of the ethyl ester of phenylacetic acid. When they used aqueous sulfuric acid (60-70%) some beta-phenylethyl ester was formed along with the beta-phenylethanol, and the yield of alcohol never exceeded 33%. The use of a benzene sulfonic acid catholyte did not increase the yield of alcohol.

Compounds such as benzene sulfonic acid are known as hydrotropes because, in aqueous solutions, they have a "salting-in" effect on added solutes. McKee and Heard (31) found that sodium benzene sulfonate exhibited hydrotropic properties toward benzyl alcohol. With a saturated sodium benzene sulfonate solution as the anolyte they were able to oxidize successfully benzyl alcohol to benzoic acid at nickel electrodes.

Aliphatic acids are much more difficult to reduce than aromatic acids. Masuno et al. (32) found that the best yield of butyl alcohol from butyric acid was 6.5% in 80% sulfuric acid and 17% in dilute sodium hydroxide.

## Apparatus

### I. Cell Design

Figure 1 shows the type of cell used for the first eighteen experiments. The set-up was about the same for all eighteen experiments except for the type of cathode (see following section).

Figure 2 illustrates the type of cell used in experiments 19 to 22 inclusive. With a soluble acid, e.g., o-bromobenzoic, it was not necessary to have the catholyte stirred, however this cell proved unsuitable for the more insoluble acids where a stirrer was needed to keep the depolariser in contact with the cathode.

Figure 3 shows the type of cell used in experiments 23-47. An extra wide slot in the cathode next to the stirrer was used to give more room for rotation of the stirrer.

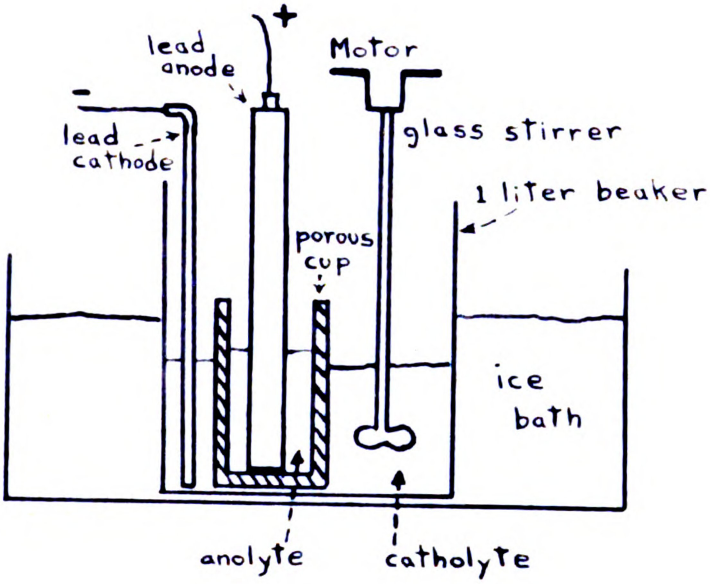

+
lead anode
Motor
-
glass stirrer
lead cathode
1 liter beaker
porous cup
ice bath
anolyte
catholyte

Figure 1

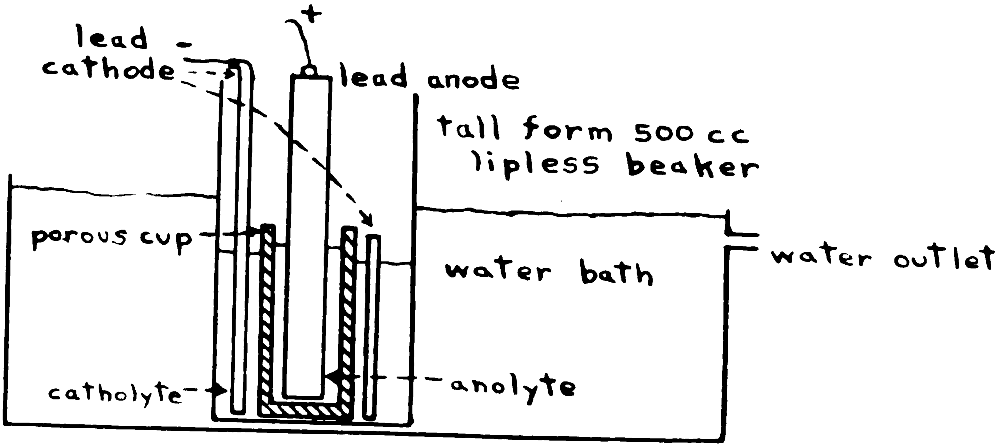


Figure 2

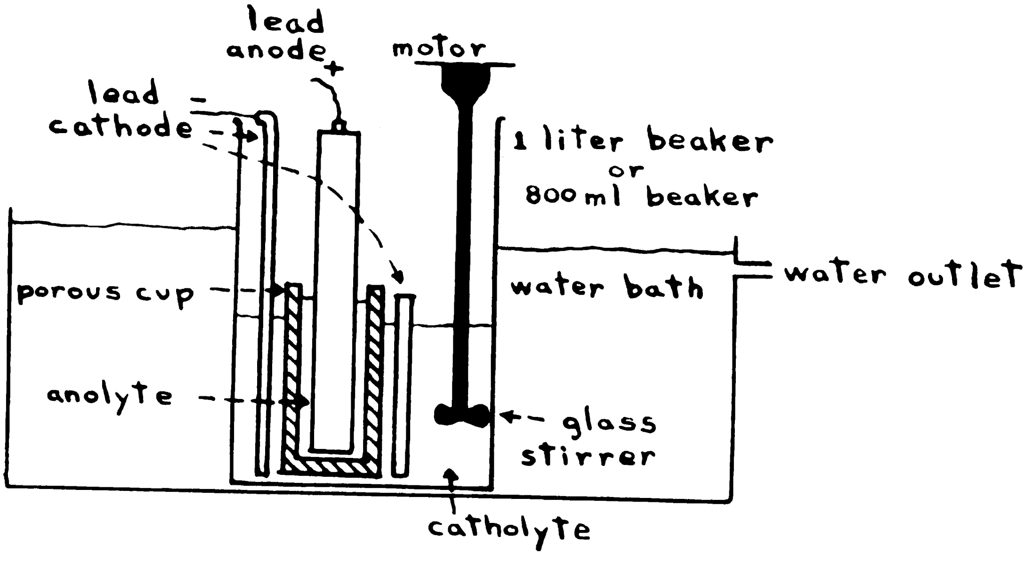


Figure 3

## II. Electrodes

The anode used in all experiments was standard quality sheet lead, 7 cm. wide and 20 cm. long, bent to form a hollow cylinder 7 cm. in circumference which would fit inside a porous cup.

In experiments 1 and 2 the sheet lead cathode shown in Figure 4-A was used. A nickel gauze cathode was used in experiment 3. The sheet lead cathode shown in Figure 4-B was used in experiments 4-18. This type of cathode was bent part way around the outside of the cup in order to decrease the internal resistance of the cell. Figure 4-C shows the type of sheet lead cathode used for experiments 19-47. This type of cathode was bent to fit almost completely around the outside of the porous cup and was slotted in order to secure better circulation of the catholyte.

The lead cathodes used in experiments 5 and 10-47 were prepared according to the method of Swann (33) by oxidizing them in sulfuric acid solution so that a layer of spongy lead dioxide was formed on the surface of the electrode.

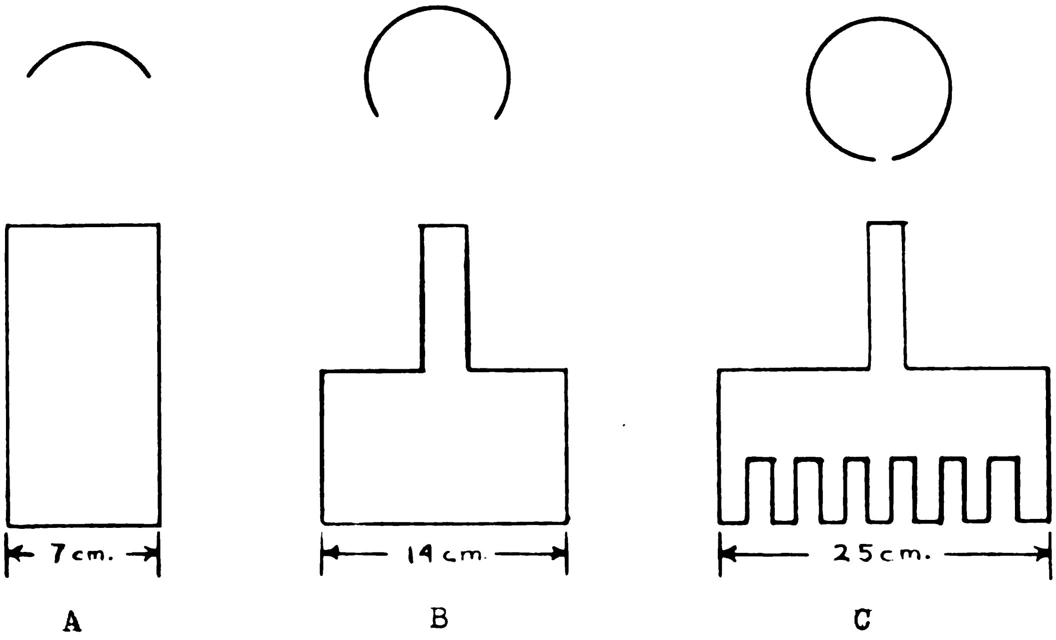


Figure 4

## III. Porous Cups

For the first eighteen experiments the cups were cleaned by sucking 20% sodium hydroxide through the walls until the cup was almost half full, emptying out the hydroxide, and then repeating the process with 20% sulfuric acid. From experiment 19 on the cups were cleaned by allowing them to remain immersed in successive portions of 20% sulfuric acid. This latter treatment is recommended by Swann (33). These cups were cleaned in order to remove iron impurities which were present.

In experiment 23 and thereafter the wash sulfuric acid was tested for ferric iron by adding potassium thiocyanate. If the test was positive the cups were again immersed in sulfuric acid and the treatment continued until a negative test was obtained.

## Laboratory Procedure

### I. Preparation of Acids

The acids used in experiments 8 to 10, 12, 17, 21 to 39, and 42 to 49 were obtained from Eastman Kodak. All were "Eastman White Label" chemicals with the exception of the 3,4-dichlorobenzoic acid which was "Practical" grade.

The ortho-bromobenzoic acid (m.p. 150°C) used in experiments 1 to 7, 15 and 18 was prepared in this laboratory by a Sandmeyer reaction similar to that used by Hodgson and Walker (35). Cuprous chloride used in the Sandmeyer reaction was made by the method of Marvel and McElvain (36). The ortho-bromobenzoic acid used in experiments 11, 13 and 16 was made by the same method as above, however, a variation in the purification of the acid was used. Instead of filtering the acidified reaction mixture at once to recover the acid, the system was first diluted by adding it slowly (with constant stirring) to three parts of water. The system was then cooled with an ice-bath and the crude acid filtered off and purified by the usual methods.

Para-bromobenzoic acid (m.p. 251°C) for use in experiment 14 was prepared by the potassium permanganate oxidation of para-bromotoluene. The method was that of Clarke and Taylor (37). This same method was utilized to make the ortho-chlorobenzoic acid (m.p. 142°C) used in experiment 19; however, in purifying the acid the usual method was changed and the reaction mixture was not concentrated before filtration.

The para-chlorobenzoic acid used in experiment 20 was a student preparation obtained from the stockroom. Its method of preparation was unknown but it was recrystallized from a 50% alcohol-water medium and had a m.p. of 243°C.

The 2,6-dichlorobenzoic acid (m.p. 143-144°C) for experiments 40 and 41 was made from 2,6-dichlorotoluene by the method of Lehmstadt and Schrader (38).

## II. Electrolytic Reduction Of Acids

The porous cup was cleaned, as previously described, filled with the anolyte, and let stand so that the anolyte would permeate the pores of the cup. In the meantime, the cathode and catholyte were prepared. If alcohol was used in the catholyte it was found best to dissolve the substituted benzoic acid in the alcohol and then cautiously add the sulfuric acid (with cooling) to the alcoholic solution.

The apparatus was assembled, the electrodes connected to the switchboard (15 volt line) and the variable resistance adjusted to obtain the desired current. Often when a fairly large current (around 10 amps) was used with an alcoholic catholyte, (with no added water) it was possible to pass only 7 or 8 amps without excessive heating of the system. However in ten or fifteen minutes the current could often be increased to 10 amps without having the temperature go above 35°C. The reaction was stopped when about three times the theoretical (based on one Faraday per equivalent weight of acid) amount of current had been passed or when increased evolution of hydrogen was noticed.

## III. Conditions For Electrolytic Reductions

Forty-nine experiments were carried out using varying conditions of current density, catholyte composition, etc. The conditions used for each experiment are listed in the tables which follow. These tables are arranged so that acids which behave similarly in electrolytic reductions are listed together. In this way comparisons of the influence of different preparative conditions are facilitated.

## TABLE I

### CONDITIONS FOR REDUCTION OF ORTHO-BROMO- AND ORTHO-CHLOROBENZOIC ACIDS USING ETHYL ALCOHOL CATHOLYTES

**All experiments were carried out with ortho-bromobenzoic acid except experiments 19 and 31 which were carried out with ortho-chlorobenzoic acid.**

| | Catholyte Composition | | | | Anolyte Composition | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Experiment | ml alc | ml $H_2O$ | ml $H_2SO_4$ | gm acid | ml $H_2O$ | ml $H_2SO_4$ | Time in Hours | Amps | Current Density Amps/$dm^2$ | Cell Voltage | Temp °C | Note |
| 1 | 320 | 80 | 54 | 35 | 80 | 20 | 5 | 11 | 11 | 7 | 25 | |
| 2 | 320 | 80 | 54 | 35 | 80 | 20 | 5 | 11 | 11 | 7 | 25 | |
| 3 | 320 | 80 | 54 | 35 | 80 | 20 | 2.5 | 25 | 11 | 6 | 25 | (1) |
| 4 | 255 | None | 45 | 35 | 65 | 15 | 5 | 4-10 | 7 | 10 | 30 | (1) |
| 5 | 230 | 25 | 45 | 35 | 60 | 10 | 6 | 10 | 7 | 7 | 25 | |
| 10 | 230 | 25 | 45 | 35 | 60 | 10 | 4.5 | 10-15 | 7-10 | 6 | 30 | (2) |
| 11 | 230 | 25 | 45 | 37 | 60 | 10 | 2.5 | 11-20 | 8-14 | 6-8 | 30-35 | (3) |
| 13 | 230 | 25 | 45 | 35 | 60 | 10 | 4 | 11 | 8 | 7 | 25-30 | |
| 15 | 230 | 25 | 45 | 25 | 60 | 10 | 3.5 | 11 | 8 | 6 | 25-30 | |
| 16 | 230 | 25 | 45 | 35 | 60 | 10 | 2.5 | 11 | 8 | 6 | 25-30 | (4) |
| 18 | 230 | 25 | 45 | 35 | 60 | 10 | 2.5 | 11 | 8 | 6 | 25-30 | (5) |
| 19 | 90 | None | 18 | 20 | 80 | 12 | 2.5 | 10 | 7 | 6 | 30 | |

## TABLE I - CONTINUED

| Experiment | Catholyte Composition ml alc. | ml $H_2O$ | ml $H_2SO_4$ | gm acid | Anolyte Composition ml $H_2O$ | ml $H_2SO_4$ | Time in Hours | Amps | Current Density Amps/$dm^2$ | Cell Voltage | Temp. °C | Note |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 28 | 135 | None | 27 | 20 | 60 | 15 | 4 | 8 | 11 | 6 | 30 | |
| 31 | 135 | None | 27 | 20 | 60 | 15 | 4.3 | 8 | 11 | 6 | 30 | |
| 42 | 135 | None | 27 | 20 | 60 | 15 | 3 | 11 | 12 | 7 | 35-40 | |
| 43 | 135 | None | 27 | 20 | 60 | 15 | 6 | 6 | 6.5 | 5 | 30-35 | |
| 44 | 135 | None | 27 | 20 | 60 | 15 | 5 | 8 | 9 | 6 | 30-35 | |
| 47 | 135 | None | 27 | 20 | 60 | 15 | 1.5 | 8 | 11 | 7 | 35 | |

1. Current was increased from 4 to 10 amps during first hour of run and then held steady.

2. Current was increased to 15 amps after 3 hours, at which time increased hydrogen evolution was noted.

3. Current was increased to 15 amps after 2 hours and 20 amps after 2.5 hours, at which time increased hydrogen evolution was noted.

4. The flow of current became very erratic after 2.5 hours and the run was stopped.

5. Cupric sulfate (0.1 gm) was added to the catholyte.

## TABLE II

### CONDITIONS FOR REDUCTION OF ORTHO-BROMO AND ORTHO-CHLOROBENZOIC ACIDS USING CATHOLYTES OTHER THAN ETHYL ALCOHOL

**All experiments were carried out with ortho-bromobenzoic acid except experiment 45 which was carried out with ortho-chlorobenzoic acid.**

| Experiment | Grams Acid | Catholyte Composition | Anolyte Composition | Time in Hours | Amps | Current Density Amps/dm$^2$ | Cell Voltage | Temp °C | Note |
|---|---|---|---|---|---|---|---|---|---|
| 6 | 39 | 300 ml 40% sodium Xylene sulfonate | 70 ml 10% $Na_2SO_4$ | 5 | 11 | 8 | 5 | 75 | (1) |
| 7 | 30 | 340 ml 37% sodium Xylene sulfonate | 100 ml 10% $Na_2SO_4$ | 5 | 9 | 5 | 7 | 30 | |
| 8 | 25 | 250 ml 50% sodium Xylene sulfonate | Same as #7 | 5.5 | 7 | 6 | 6 | 30 | (2) |
| 9 | 22.5 | 300 ml 40% sodium Xylene sulfonate | 130 ml 10% $Na_2SO_4$ | 3 | 7 | 5 | 6 | 30 | (3) |
| 38 | 10 | 10 gm NaAc 90 ml $H_2O$ 90 gm t-butyl alcohol | 60 ml $H_2O$<br>10 gm NaAc | 1.5 | 4-8 | 5-9 | 7-10 | 35 | (4) |
| 45 | 10 | 27 ml $H_2SO_4$<br>135 ml Methyl Cellosolve | 60 ml $H_2O$<br>15 ml $H_2SO_4$ | 2 | 7 | 9 | 8 | 35-40 | (5) |

1. No cooling bath was used. The flow of current was erratic.

2. Excessive frothing of the sodium xylene sulfonate catholyte occurred at first. More water (50 ml) was then added to reduce the concentration of the catholyte and stop the frothing.

3. Flow of current was stopped in 3 hours by a heavy crust on the outside of the porous cup.

4. Anode was severely attacked by the anolyte. Corrosion products plugged the inside of the porous cup.

5. The catholyte was not as good a conductor of current as an alcoholic catholyte.

## TABLE III

### CONDITIONS FOR REDUCTION OF META- AND PARA-HALOBENZOIC (BROMO AND CHLORO) ACIDS

| Experiment | Acid | | Catholyte Composition | | Anolyte Composition | | Time in Hours | Amps | Current Density Amps/$dm^2$ | Cell Voltage | Temp. °C | Note |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gm | Kind | ml alc. | ml $H_2SO_4$ | ml $H_2O$ | ml $H_2SO_4$ | | | | | | |
| 14 | 44 | p-bromo | 230 | 45 | 60 | 10 | 5 | 11 | 8 | 7 | 25-30 | 1 |
| 20 | 20 | p-chloro | 90 | 18 | 80 | 12 | 7 | 6 | 4 | 4 | 35 | 2 |
| 21 | 20 | p-bromo | 90 | 18 | 80 | 12 | 4.8 | 6 | 4 | 6 | 45 | |
| 22 | 20 | p-chloro | 90 | 18 | 80 | 12 | 4.8 | 10 | 7 | 4 | 30-35 | 3 |
| 23 | 30 | p-chloro | 135 | 27 | 80 | 20 | 5 | 6 | 8 | 5-6 | 30-40 | |
| 24 | 20 | p-chloro | 135 | 27 | 60 | 15 | 6.3 | 7 | 9 | 5-6 | 30 | |
| 25 | 20 | m-bromo | 135 | 27 | 60 | 15 | 4.5 | 7 | 9 | 7 | 35-40 | |
| 26 | 20 | p-chloro | 135 | 27 | 60 | 15 | 6.8 | 8 | 11 | 6 | 30 | |
| 27 | 20 | m-chloro | 135 | 27 | 60 | 15 | 5.5 | 6 | 8 | 7 | 35 | |
| 29 | 20 | p-bromo | 135 | 27 | 60 | 15 | 6 | 8 | 11 | 7 | 30-35 | |
| 30 | 20 | m-bromo | 135 | 27 | 60 | 15 | 5 | 7 | 9 | 8 | 35 | |
| 46 | 10 | p-bromo | 220 | 20 | 60 | 15 | .8 | 13 | 9 | 8 | 40-45 | |

1. Water (25 ml) was used to help make up the catholyte.
2. A 7.5 volt line was used instead of the usual 15 volt line.
3. Excessive discharge of hydrogen at the cathode was noticed.

## TABLE IV

## CONDITIONS FOR REDUCTION OF IODOBENZOIC ACIDS

**The anolyte in all experiments was composed of 60 ml.of water, and 15 ml. of $H_2SO_4$. The catholyte in all experiments contained 20 grams of iodobenzoic acid.**

| Experiment | Acid | Catholyte Composition | | Time in Hours | Amps | Current Density Amps/dm$^2$ | Cell Voltage | Temp. $^oC$ |
|---|---|---|---|---|---|---|---|---|
| | | ml Alc. | ml $H_2SO_4$ | | | | | |
| 33 | m-iodo | 135 | 27 | 3.5 | 5 | 7 | 7 | 35 |
| 35 | p-iodo | 135 | 27 | 3.3 | 8.5 | 11 | 6 | 30 |
| 48 | m-iodo | 180 | 35 | 5.5 | 8 | 11 | 8 | 30-35 |
| 49 | p-iodo | 180 | 35 | 3.5 | 8 | 11 | 7 | 35 |

## TABLE V

## CONDITIONS FOR REDUCTION OF DICHLOROBENZOIC ACIDS

**The anolyte in all experiments was composed of 60 ml. of water and 15 ml. of $H_2SO_4$.**

| Experiment | Acid | | Catholyte Composition | Time in Hours | Amps | Current Density Amps/dm$^2$ | Cell Voltage | Temp. °C | Note |
|---|---|---|---|---|---|---|---|---|---|
| | gm | Kind | | | | | | | |
| 36 | 20 | 2,4-dichloro | 135 ml alcohol<br>27 ml $H_2SO_4$ | 3.3 | 6 | 8 | 7 | 35 | 1 |
| 37 | 10 | 3,4-dichloro | 200 ml alcohol<br>30 ml $H_2SO_4$ | 3 | 9 | 7 | 8 | 35 | |
| 39 | 10 | 3,4-dichloro | 135 ml n-propyl alcohol<br>20 ml $H_2SO_4$ | 1.8 | 7-9 | 9-12 | 8-10 | 35-40 | 2 |
| 40 | 10 | 2,6-dichloro | 200 ml alcohol<br>35 ml $H_2SO_4$<br>30 ml $H_2O$ | 4 | 10 | 6 | 5 | 30-35 | |
| 41 | 10 | 2,6-dichloro | 135 ml alcohol<br>27 ml $H_2SO_4$ | 4 | 10 | 13 | 7 | 35-40 | |

1. **The catholyte was very viscous.**

2. **The catholyte was notas** good **a conductor of current as an alcoholic catholyte.**

## TABLE VI

## CONDITIONS FOR REDUCTION OF PARA-TOLUIC AND ANISIC ACIDS

**All experiments were carried out with p-toluic acid except experiment 32 which was carried out with anisic acid**

| | Catholyte Composition | | | | Anolyte | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | ml alc. | ml $H_2O$ | ml $H_2SO_4$ | gm acid | ml $H_2O$ | ml $H_2SO_4$ | Time in Hours | Amps | Current Density Amps/$dm^2$ | Cell Voltage | Temp. °C | Note |
| 12 | 230 | 25 | 45 | 35 | 60 | 10 | 5.5 | 11-14 | 8-10 | 6-7 | 25-30 | 1 |
| 17 | 230 | 25 | 45 | 30 | 60 | 10 | 4 | 11 | 8 | 6 | 25-30 | 2 |
| 32 | 135 | None | 27 | 20 | 60 | 15 | 4 | 8 | 11 | 7 | 30-35 | |
| 34 | 135 | None | 27 | 20 | 60 | 15 | 2 | 8 | 11 | 6 | 30 | |

1. It was necessary to use a 7.5 volt line for 1.5 hours during the run because the 15 volt line was cut off after the run started.

2. Cupric sulfate (0.2 gm) was added to the catholyte. During the run some copper plated out on the cathode.

## IV. Purification Of Alcohols

Ammonium hydroxide (1 part concentrated $NH_4OH$ to 1 part water) was added to the catholyte until basic to litmus, after which 10 ml. were added to insure an excess. The system divided into two liquid phases and was placed in a separatory funnel. The bottom layer (aqueous) was then drawn off and 400 ml. of water added, after which it was acidified with 10% sulfuric acid until blue to Congo red paper. Any unreduced acid precipitated and was recovered by suction filtration.

Water was slowly added to the top (alcoholic) layer, with stirring, until the cloud point was reached. The system was then set aside overnight to let the alcohol crystallize. When most of the alcohol appeared to have crystallized, 300 ml. of water was added, the mixture cooled in an ice bath and filtered by suction while cold. The precipitate was washed with 150 ml. of 10% sodium hydroxide to remove any acid impurities, filtered and then recrystallized from an alcohol-water (50%) medium.

If the substituted benzyl alcohol being isolated was a liquid at room temperature it settled out when the top alcoholic layer of the original two phase system was diluted with water and let stand overnight. The crude alcohol was then removed by a separatory funnel, anhydrous sodium sulfate added, and the alcohol dried overnight. The dried alcohol was then vacuum distilled using conventional equipment.

A different scheme of purification was employed in the experiments where solutions of sodium xylene sulfonate were used as catholytes. This was necessary because the hydrotropic ("salting in") properties of the sodium xylene sulfonate would make isolation of the alcohol difficult by the usual method.

In experiment 6 the reaction mixture was diluted with two parts of water, 10% NaOH added until alkaline, and extracted with petroleum ether. Low-temperature evaporation of petroleum ether left no residue. Upon acidification of the aqueous solution a white precipitate "A" separated, was removed by filtration, and dried. The filtrate was evaporated at room temperature to one liter, make alkaline with NaOH, and then NaCl added until the solution was saturated. On stirring for six hours a voluminous precipitate separated. Water (400 ml.) and 25 grams of NaOH were added to the precipitate and the mixture steam distilled. There was no evidence of any ortho-bromobenzyl alcohol in the distillate. The precipitate "A" (found to be benzoic acid) was dissolved in NaOH solution, the system acidified, filtered and the residue dried. The benzoic acid was then recrystallized from an alcohol-water (50%) medium. The descriptions of the methods of purification used in experiments 7, 8, and 9 are omitted as the procedures were very long, resulted in no isolated substance which melted below 300°C, and were abandoned after benzoic acid was isolated from the catholyte used in experiment 6.

## RESULTS

The results of the various experiments are listed in the tables which follow. The experiments are grouped in these tables the same as they were grouped in the tables giving the conditions for electrolytic reductions.

It was found that when the yield of alcohol is small a large portion of the unreacted acid was usually recovered. In the cases where the amount of recovered acid was listed in the record book, the number of grams is given in the tables.

The carbon, hydrogen, and halogen determinations of the various benzyl alcohols were made by the Clark Microanalytical Laboratory, Urbana, Illinois.

## TABLE VII

### RESULTS OF ORTHO-BROMO- AND ORTHO-CHLOROBENZOIC ACIDS USING ETHYL ALCOHOL CATHOLYTES

**All experiments were carried out with ortho-bromobenzoic acid except experiments 19 and 31 which were carried out with ortho-chlorobenzoic acid**

**Literature m.p. of ortho-bromobenzyl alcohol is** 80°C
**Literature m.p. of ortho-chloro is 74°C**

| Exp. | Yield Of Alcohol In Grams | Chemical Yield (%) | Current Efficiency (%) | m.p. Of Alcohol °C | Recovered Acid (gm) | Note |
|---|---|---|---|---|---|---|
| 1 | 9 | 28 | 9 | 79° | 18.5 | |
| 2 | 7 | 22 | 7 | 80° | 15 | |
| 3 | 0 | 0 | 0 | - | 16 | |
| 4 | 4.7 | 15 | 6 | 79° | 12.5 | |
| 5 | 9 | 28 | 9 | 79° | 12.3 | |
| 10 | 22.8 | 70 | 31 | 79° | 10 | |
| 11 | 22.6 | 66 | 44 | 80° | 5 | |
| 13 | 19 | 59 | 25 | 79.5° | - | |
| 15 | 0 | 0 | 0 | - | 11.8 | |
| 16 | 6.9 | 21 | 14 | 80° | - | |
| 18 | 0 | 0 | 0 | - | 16.8 | |
| 19 | 12.3 | 68 | 37 | 71° | - | 1 |
| 28 | 12.5 | 67 | 22 | 80° | - | |
| 31 | 10 | 55 | 22 | 71°-72° | - | |
| 42 | 13.4 | 72 | 23 | 80° | - | |
| 43 | 0 | 0 | 0 | - | - | |

TABLE VII - CONTINUED

| Exp. | Yield Of Alcohol In Grams | Chemical Yield (%) | Current Efficiency (%) | m.p. Of Alcohol °C | Recovered Acid (gm) | Note |
|---|---|---|---|---|---|---|
| 44 | 7.5 | 40 | 10 | 80° | - | 2 |
| 47 | 0 | 0 | 0 | - | - | |

1. A sample of this alcohol was recrystallized from toluene to a constant m.p. of 72°C.

2. A sample of this alcohol was recrystallized from alcohol-water (50%) to a constant m.p. of 80°C.

## TABLE VIII

## RESULTS OF ORTHO-BROMO AND ORTHO-CHLOROBENZOIC ACIDS USING CATHOLYTES OTHER THAN ETHYL ALCOHOL

**All experiments were carried out with ortho-bromobenzoic acid except experiment 45 which was carried out with ortho-chlorobenzoic acid**

| Exp. | Yield Of Alcohol In Grams | Chemical Yield (%) | Current Efficiency (%) | m.p. Of Alcohol °C | Note |
|---|---|---|---|---|---|
| 6 | 0 | 0 | 0 | - | 1 |
| 7 | 0 | 0 | 0 | - | |
| 8 | 0 | 0 | 0 | - | |
| 9 | 0 | 0 | 0 | - | |
| 38 | 0 | 0 | 0 | - | |
| 45 | 2.2 | 24 | 12 | 71° | |

1. Dehalogenation occurred and benzoic acid (m.p. 119-120°C, lit. - 120°C) was isolated. This was proved to be benzoic acid by the method of mixed melting points.

## TABLE IX

## RESULTS OF META- AND PARA-HALOBENZOIC (BROMO AND CHLORO) ACIDS

Literature m.p. of para-bromobenzyl alcohol is 77°C
Literature m.p. of para-chlorobenzyl alcohol is 75°C
Literature b.p. of meta-bromobenzyl alcohol is 252-253° at 711 m.m.
Literature b.p. of meta-chlorobenzyl alcohol is 234°C at 760 m.m.

| Exp. | Acid | Yield Of Alcohol In Grams | Chemical Yield (%) | Current Efficiency (%) | m.p. Of Alcohol °C | Note |
|---|---|---|---|---|---|---|
| 14 | p-bromo | 0 | 0 | 0 | - | 1 |
| 20 | p-chloro | 0 | 0 | 0 | - | 2 |
| 21 | p-bromo | 4.4 | 24 | 9 | 77-77.5° | 3 |
| 22 | p-chloro | .6 | 3 | 1 | 71-72° | |
| 23 | p-chloro | 1.6 | 6 | 4 | 72-73° | |
| 24 | p-chloro | 3.8 | 21 | 7 | 71.5° | |
| 25 | m-bromo | 7.6 | 41 | 14 | b.p. (11 mm.) 131-3° | |
| 26 | p-chloro | 9.5 | 52 | 13 | 72° | 4 |
| 27 | m-chloro | 8.7 | 48 | 20 | b.p. (10 mm.) 114-8° | 5 |
| 29 | p-bromo | 12.3 | 66 | 15 | 77-78° | |
| 30 | m-bromo | 12.5 | 67 | 20 | b.p. (2 mm.) 110-2° | 6 |
| 46 | p-bromo | .3 | 3 | 2 | 77° | |

1. Acid recovered = 35 grams

2. Acid recovered = 18.5 grams

3. Acid recovered = 8.6 grams. A sample of this alcohol was recrystallized from alcohol-water (50%) to a constant m.p. of 77.5°C.

TABLE IX - CONTINUED

4. A sample of this alcohol was recrystallized from toluene to a constant m.p. of 73°C.

5. A sample of this alcohol analyzed 21.8% chlorine (Calculated = 24.9%). The product was then redistilled (b.p. 110°C at 4 mm.) and a sample of this purified alcohol analyzed 24.7% chlorine.

6. A sample of this alcohol analyzed 43.9% bromine (Calculated = 42.8%).

## TABLE X

## RESULTS OF IODOBENZOIC ACIDS

Experiments 33 and 48 were carried out with m-iodobenzoic acid
Experiments 35 and 49 were carried out with p-iodobenzoic acid
Literature b.p. of meta-iodobenzyl alcohol is 165°C at 16 mm.
Literature m.p. of para-iodobenzyl alcohol is 72-73°C.

| Exp. | Yield Of Alcohol In Grams | Chemical Yield (%) | Current Efficiency (%) | m.p. Of Alcohol °C | Note |
|---|---|---|---|---|---|
| 33 | 5.4 | 29 | 13 | b.p.<br>(5 mm.)<br>117-22° | |
| 35 | .7 | 4 | 1 | 71-72° | |
| 48 | 4.3 | 23 | 5 | See Note | 1 |
| 49 | .6 | 4 | 1 | 73° | 2 |

1. The crude product was distilled using a small fractionating column and the following fractions collected:

Fraction 1 = 1 gm., up to 115°C at 3 mm.,
D = 1.5630 at 27°C
Fraction 2 = 1.9 gm., 115-124°C at 3 mm.,
D = 1.5843 at 27°C
Fraction 3 = 2.4 gm., 124°C at 3 mm.,
D = 1.5843 at 27°C
Pot Residue = 4.2 gm.

The refractive index (D) of meta-iodobenzyl alcohol could not be found in the literature.

The weights of fractions 2 and 3 were used in calculating the yield of m-iodobenzyl alcohol. The usual method of purification did not yield any unreacted meta-iodobenzoic acid.

Analysis of this product (fraction 3) gave 51.7% iodine (calculated 51.2%).

2. The unreacted acid recovered in this experiment weighed 6.1 grams.

## TABLE XI

## RESULTS OF DICHLOROBENZOIC ACIDS

| Exp. | Acid Used | Yield Of Alcohol In Grams | Chemical Yield (%) | Current Efficiency (%) | m.p. Of Alcohol °C |
|---|---|---|---|---|---|
| 36 | 2,4-dichloro | 0 | - | - | - |
| 37 | 3,4-dichloro | 0 | - | - | - |
| 39 | 3,4-dichloro | 0 | - | - | - |
| 40 | 2,6-dichloro | 0 | - | - | - |
| 41* | 2,6-dichloro | .5 | 6 | 2 | 102° |

* The m.p. of 2,6-dichlorobenzyl alcohol could not be found in the literature. A sample of this product gave the following analysis:

Carbon - 47.6% (calculated 47.5%)
Hydrogen - 3.53% (calculated 3.53%)
Chlorine - 39.8% (calculated 40.1%)

## TABLE XII

## RESULT OF PARA-TOLUIC AND ANISIC ACIDS

Literature b.p. of anisyl alcohol:127-130°C at 8 mm.

| Exp. | Acid Used | Yield Of Alcohol In Grams | Chemical Yield (%) | Current Efficiency (%) | Note |
|---|---|---|---|---|---|
| 12 | p-toluic | 0 | - | - | 1 |
| 17 | p-toluic | 0 | - | - | 2 |
| 32 | anisic | 2.7 | 15 | 6 | 3 |
| 34 | p-toluic | 0 | - | - | 4 |

1. Acid recovered = 32 grams.

2. Acid recovered = 23 grams.

3. The b.p. of the anisyl alcohol is 124-6°C at 9 mm.

4. A crude yield of 2.8 grams was obtained but this was lost during purification of the alcohol.

## DISCUSSION

The Mettler method appears to be a satisfactory procedure for the preparation of the mono-chloro - and mono-bromobenzoic acids. The best chemical yields and current efficiencies are obtained with ortho-bromo - and ortho-chlorobenzoic acids, probably because the ortho acids are more soluble in the usual alcohol-sulfuric acid catholyte than the meta and para isomers are. Since the ortho-bromo - and ortho-chlorobenzyl alcohols are the most difficult of the mono isomers to prepare by the usual organic chemical methods, electrolytic reduction of the acids appears to be particularly desirable for the synthesis of these alcohols.

The chemical yields of the meta - and para-monohalobenzoic (bromo and chloro) alcohols are slightly lower than the chemical yields of the corresponding ortho isomers. However the current efficiencies of the meta and para alcohols are much lower than those obtainable with the ortho isomers. The decreased solubility of the meta and para acids in an alcohol-sulfuric acid catholyte is probably responsible for the great difference in current efficiencies. Since it is not possible to purify the liquid meta alcohols by the same method as the solid ortho and para alcohols, it is difficult to compare the yields of the three isomers.

The usefulness of the Mettler method for the preparation of meta - and para-iodobenzyl alcohols is limited by the relative insolubility of the iodo acids, para-iodobenzoic acid being the most insoluble of the two. For example in experiment 35 the catholyte was so viscous (due to undissolved para-iodobenzoic acid) that it was almost a gel. This decreased solubility is probably responsible for the low yields obtained with the iodo acids, the yield of the para isomer being particularly poor.

Experiments were carried out with three dichlorobenzoic acids, the 2,4-, 3,4- and 2,6-dichlorobenzoic acids. These acids are less soluble than the mono acids and this decreased solubility is again thought to be responsible for the poor results obtained. It is interesting to note that the only dichloro acid (2,6 isomer) which was successfully reduced was the most soluble of the three dichloro acids used.

A lead dioxide cathode appears to be more suitable for these reductions than a plain lead cathode, although some reduction will take place with a plain lead cathode. A nickel cathode does not appear to be suitable for the reduction of these benzoic acids, probably because of its lower overvoltage.

Iron salts in the porous cups are known to retard (2) the reduction of benzoic acids. These salts were found to be present in the cups used in this work. The cups were washed in all experiments to remove the iron salts, however from experiment 23 on the washing was continued until a negative test for ferric iron was obtained. It seems probable that the better yields obtained from experiment 23 on are due to the complete removal of the inhibiting iron salts.

Copper salts were added to the catholytes used in experiments 17 and 18 in the hope that they might promote the reduction of the acids. The presence of the copper salts did not appear to help the reduction.

A high current density (10-12 amps/sq.dm.) appears to be the most suitable, although good yields of alcohols were obtained in isolated cases with current densities as low as 7 amps/sq.dm. and as high as 15 amps/sq.dm. At current densities below 6 amps/sq.dm. the reduction proceeds very poorly and the yields are very low. The use of very high current densities appears to be limited by the fact that excessive overheating of the catholyte occurs with the large amount of current used.

The influence of current density on the chemical yield can be seen in experiments 42, 43, and 44. These experiments were carried out under similar conditions, the time of current passage being adjusted to give approximately the same number of ampere hours.

TABLE XIII

INFLUENCE OF CURRENT DENSITY ON CHEMICAL YIELD OF ALCOHOLS

| | Chemical Yield (%) | Current Density (Amps/sq.dm.) |
|---|---|---|
| Exp. 42 | 72 | 12 |
| Exp. 43 | 0 | 6 |
| Exp. 44 | 40 | 9 |

It is necessary to pass a large excess of current in order to secure good yields of the alcohols. In the cases where a small excess of current was used the yields of alcohols were poor and a large excess of current was used in all experiments where good yields were obtained. The use of such a large excess of current results in poor current efficiencies for this method of electrolytic reduction. In no instance was the current efficiency better than 44% and in most cases it was considerably lower.

The use of an ethanol-sulfuric acid catholyte appears to be the most satisfactory. Higher alcohols and "Methyl Cellosolve" do not appear to be suitable for this type of electrolytic reduction. From the standpoint of solubility a sodium xylene sulfonate catholyte appears to be satisfactory, however with this catholyte dehalogenation of the aromatic ring occurs and benzoic acid is obtained.

It is not known why such poor results were obtained in experiments 46 and 47, although it is suspected that excessive use of the cathode had resulted in a loss of its activity. The cathode appeared to have a large amount of lead sulfate formed on the surface and according to Swann and Lucker (16) this is one of the characteristics of lead cathodes which have lost their activity due to prolonged use.

## CONCLUSIONS

1. High current densities are necessary for the successful electrolytic reduction of these substituted benzoic acids.

2. The most suitable catholyte of those tried is an alcohol-sulfuric acid mixture.

3. Washing the porous cups with sulfuric acid until the cups are free of iron impurities will improve the yield of substituted benzyl alcohol and increase the current efficiency.

4. The chemical yields of the benzyl alcohols and current efficiencies depend upon the relative solubility of the corresponding benzoic acid in an alcohol-sulfuric acid catholyte. In general, the more soluble the benzoic acid, the better the chemical yield of the benzyl alcohol and the higher the current efficiency.

5. Electrolytic reduction of the acid is a desirable method of preparation for the mono chloro and bromo alcohols.

6. This method of reduction appears to be of limited application for the preparation of iodo and dichloro alcohols because of the relative insolubility of the acid in alcohol-sulfuric acid catholyte.

7. Para-bromo- and para-iodobenzyl alcohol have been prepared for the first time by electrolytic reduction

of the corresponding benzoic acids.

8. A new compound, 2,6-dichlorobenzyl alcohol has also been prepared by electrolytic reduction of the acid.

# REFERENCES

1. Fichter, F., "Organische Elektrochemie", Vol. VI of "Die Chemische Reaktion", Bonhoeffer, K. F. - editor, Theodor Steinkopff, Dresden and Leipzig, 1942, pp. 253-260.
2. Mettler, C., Ber. 39, 2933-2942 (1906).
3. Mettler, C., Ber. 38, 1745-1753 (1905).
4. Mettler, C., Ger. Pat. 177,490; C.A. 1, 1211 (1907).
5. Wu, D. Y., Master's Thesis Michigan State College (1949) pp. 9-13 and 39.
6. Mettler, C., Ber. 37, 3692-3696 (1904).
7. Mettler, C., Ger. Pat. 166,181; Chem. Zentr. 77-I, 615 (1906).
8. Tafel, J. and Friedrichs, G., Ber. 37, 3187 (1904).
9. Tafel, J., Ber. 33, 2209-2224 (1900).
10. Tafel, J., and Naumann, K., Z. physik. Chem. 50, 713-752 (1905).
11. Inoue, H., J. Chem. Ind. (Japan) 24, 906-18 (1921); C.A. 16, 2320 (1922)
12. Decans, V., and Dufour, J., Bull. soc. chim. (4) 37, 1167-1174 (1925)
13. Baur, E., and Muller, E., Z. Elektrochem. 34, 98-103 (1928).
14. Somlo, F., Z. Elektrochem. 35, 264-265 (1929).
15. Fichter, F., and Stein, I., Helv. Chim. Acta 12, 821-826 (1929); C.A. 23, 4613 (1929).
16. Swann, S. and Lucker, G. D., Trans. Electrochem. Soc. 75, 411-426 (1939).
17. Nithack, R., Ger. Pat. 123,554; Chem. Zentr. 72-II, 715 (1901).

18. Weil, H., Ger. Pat. 196,239; Chem. Zentr. 79-I, 1504 (1908).

19. Mettler, C., Ber. 41, 4148-4150 (1908).

20. Tesh, K. S., and Lowy, A., Trans. Electrochem. Soc. 45, 37-45 (1924).

21. Rutovskii, B. N., and Korolev, A. I., Trans. Sci. Chem. Pharm. Inst. (U.S.S.R.) 19, 177-179 (1928); C.A. 24, 24 (1930).

22. Somlo, F., Z. Elektrochem. 35, 769-780 (1929).

23. Olivier, S. C., Rec. Trav. Chim. 43, 872-873 (1924).

24. Olivier, S. C., Rec. Trav. Chim. 41, 305 (1922).

25. Mayer, F., and English, F. A., Ann. 417, 69-70 (1918).

26. Mayer, F., Schafer, W., and Rosenbach, J., Arch. Pharm. 267, 571-584 (1929); C.A. 24, 838 (1930).

27. Coleman, G. H., and Johnson, H. L., "Organic Syntheses", Vol. 21, Drake, N. L. - editor, John Wiley and Sons, Inc., New York (1941) p. 10.

28. Kling, K., Anz. Akad. Wiss. Krakau 1908, 632; Fichter, F., "Organische Elektrochemie", Op. cit., pp. 257-258.

29. Kling, K., Anz. Akad. Wiss. Krakau 1907, 448; Fichter, F., "Organische Elektrochemie", Op. cit., p. 258.

30. Marie, C., and Marquis, R., Bull. soc. chim. (4) 25, 512-516 (1919).

31. McKee, R. H., and Heard, J. R., Trans. Electrochem. Soc. 65, 301-325 (1934).

32. Masuno, M., et al., J. Chem. Soc. Japan, Ind. Chem. Sect. 52, 151-152 (1949); C.A. 45, 1884 (1951)

33. Swann, S., et al., "Technique of Organic Chemistry" Vol. II, Weissberger, A. - editor, Interscience, New York (1948) p. 171.

34. Swann, S., et al., ibid., pp. 160-161.

35. Hodgson, H. H., and Walker, J., J. Chem. Soc. 1933, 1621.

36. Marvel, C. S., and McElvain, S. M., "Organic Syntheses", Vol. III, Clarke, H. T., editor, John Wiley and Sons, Inc., New York (1923) p. 33.

37. Clarke, H. T. and Taylor, E. R., "Organic Syntheses", Vol. X, Clarke, H. T., editor, John Wiley and Sons, Inc., New York (1930) pp. 20-21.

38. Lehmstadt, K., and Schrader, K., Ber. 70, 1530 (1937).