

The Electrolytic Reduction of Salicylic and Acetylsalicylic Acids to the Corresponding Aldehydes¹

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ABSTRACT

The electrolytic method for reducing salicylic acid to salicylaldehyde has been re-investigated, and the apparatus and procedure recommended by Tesh and Lowy has been used as a standard with which to compare new evidence. Sodium bisulfite was used for fixation of the aldehyde and a 15°–18°C reaction temperature was maintained.

The results of Tesh and Lowy, which have been questioned by some investigators, were substantiated. The necessity for using boric acid in the catholyte was shown and the possibility of using a different type of apparatus was demonstrated.

The method has been applied to acetylsalicylic acid to produce acetylsalicylaldehyde in 25 to 30 per cent yield.

INTRODUCTION

Salicylaldehyde, or o-hydroxybenzaldehyde, is manufactured on a rather substantial scale as an intermediate in the synthesis of the important perfume and flavoring material, coumarin. Two processes are currently employed in the industry to produce this aldehyde. The oldest method consists of treating phenol with chloroform and sodium hydroxide. A mixture of ortho- and para-isomers is obtained in which the ortho predominates and can be separated from the para-isomer by steam distillation. Also encountered industrially is the process starting with ortho-cresol, which is somewhat analogous to the process by which benzaldehyde is made from toluene. Coumarin is subsequently prepared from salicylaldehyde by the Perkin reaction.

Since salicylic acid is a relatively cheap material and is readily obtainable, a process for reducing this material directly to salicylaldehyde would obviously be quite desirable. The reduction of an acid to the corresponding aldehyde is, however, attended by many difficulties, and the only process of this kind of any importance involves the reduction (in water solution) of the sodium salt of the particular acid with sodium amalgam, which may be produced continuously electrolytically using a mercury cathode. This method, however, has the advantage over the Reimer-Tiemann method in giving the single desired isomer, and the yield is also improved.

The literature cites several examples pertaining to the preparation of benzaldehyde and salicylaldehyde by this method (7, 10, 12, 14, 15) as well as by the purely chemical process (1, 16) wherein metallic sodium is introduced directly into mercury to produce the amalgam.

The earliest reference to the electrolytic reduction of salicylic acid to salicylaldehyde appears to be a process patented by Hugo Weil in 1906 (15). Two years later Carl Mettler (10) described a process almost identical to Weil's for electrolytically reducing the sodium salts of benzoic and salicylic acids to the corresponding aldehydes in 30 to 50 per cent yield. Another contribution by Weil in 1908 described a process (16) using 2 per cent sodium amalgam; a yield of 60 per cent was claimed. Davies and Hodgson (1) report a 64 per cent yield of salicylaldehyde.

The most complete and thorough research carried out to date on the electrolytic reduction of salicylic acid to salicylaldehyde has been that of Tesh and Lowy (14), who reported that by following Mettler's specifications they were able to obtain a yield of only 20 per cent. To increase this yield and to work out the details of the process which had been omitted by both Weil and Mettler, Tesh and Lowy undertook an extensive study of the numerous variables involved. Their most significant contribution was to recommend the use of sodium bisulfite to combine with the newly-formed aldehyde to protect it from further reduction to the alcohol. Their best yield was reported as 55 per cent. (Because they used a molecular weight of 140, rather than 138.12, this

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yield should be reduced to 54.2 per cent and other values should be reduced by the same factor.)

Rutovskii and Korolev (12) reported in 1928, on testing the electrolytic reduction of salicylic acid according to Weil and also Tesh and Lowy, that the methods gave yields only up to 34 per cent of the theory and then only if all experimental conditions were strictly observed. They also pointed out that stirring is of great importance. Kawada and Yosida (7) have reported on a similar procedure wherein the only significant difference was the addition of borax to the catholyte, but a yield of 80 per cent was claimed. These several papers reporting such a wide variation in yield of this important chemical intermediate call for a reinvestigation to determine if an 80 per cent yield can be obtained. It was further desired to carry out this reduction on acetylsalicylic acid (aspirin), since the corresponding aldehyde might be expected to yield coumarin directly through dehydration.

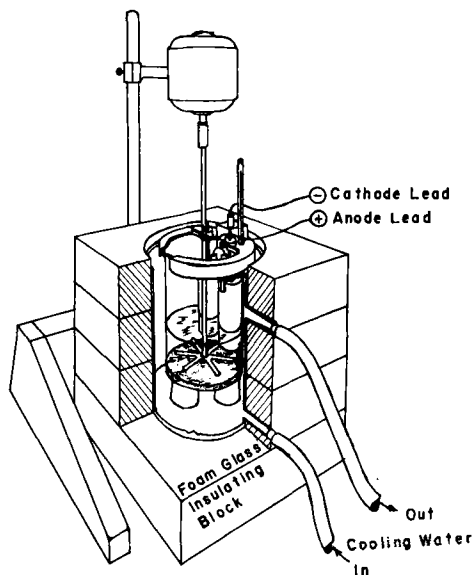


FIG. 1. Basic or standard reduction cell

APPARATUS

Basic or Standard Reduction Cell

The major portion of the experimental work of this research was carried out in apparatus which differed only in minor details from that described by Tesh and Lowy. The electrolytic cell consisted of a 600 ml beaker in the bottom of which was placed 25 ml of mercury to serve as the cathode. Lead strips were employed as anodes, and the anolyte was contained in two porous cups [1 in. x 2.75 in. (2.5 x 7 cm) alundum extraction thimbles], which served also as diaphragms and were suspended so that the bottom of each was two centimeters above the surface of the mercury. Additional details are shown in Fig. 1.

Modifications in the Basic Apparatus

The basic apparatus just described was modified to a greater or lesser extent in several experiments to explore a few of the possibilities for design of full scale equipment. Two distinctly different possibilities exist. First, a cell consisting of all the conventional elements might be retained in which case the prime consideration would be the reduction in the quantity of mercury required. Second, equipment might be designed in which the amalgam would be generated in a separate cell similar to the German vertical cell (2) or the Mathieson Chemical Corporation cell (3), and the reduction would subsequently be carried out in a separate reactor or decomposing tower.

In the first case, experiments were conducted by substituting a thoroughly cleaned and amalgamated sheet of lead or iron for the mercury layer. In the case of the sheet iron, a mercury film or amalgam was obtained only after, but immediately upon, passage of current. Any excess of mercury was then decanted from the metal.

In the second case, an electrolytic cell similar to and of the same size as the basic cell was set up to produce sodium amalgam for use in a fixed surface (beaker) type reactor with stirrer or in a 16 mm jacketed glass tubing decomposing tower or reactor packed with 2 ft (61 cm) of 3 mm glass beads through which the amalgam and reaction mixture were passed counter-currently. A bottom drawoff tube with an adjustable seal leg maintained a constant mercury level in the cell by forwarding amalgam to the reactor as the denuded mercury was manually returned to the cell at a rate of about 2 ml per minute.

One further modification of the Tesh-Lowy apparatus was made for the express purpose of raising the yield, and in this instance, the electrical circuit alone was changed. It was thought that the yield and current efficiency might be improved if a better balance could be struck between the rate of reaction and the rate of electrolysis. To accomplish this end, a simple commutator was introduced into the circuit to furnish an interrupted or intermittent direct current.

EXPERIMENTAL PROCEDURE

The procedure followed in a majority of the experiments of the present research involved only minor changes from the Tesh-Lowy method. To 155 ml of distilled water there were added, in the order listed, with stirring until each constituent dissolved, 4.0 grams (0.1 mole) sodium hydroxide, 14.0 grams (0.103 mole) salicylic acid, 15.0 grams sodium sulfate, and 15.0 grams boric acid. Unless otherwise indicated in Table I, a total of 20 grams sodium bisulfite were also added to the above catholyte mixture at 10 minute intervals during the electrolysis.

The anolyte consisted of 25 ml of 10 per cent sodium sulfate solution.

When aspirin was investigated, 18.0 grams (0.1 mole) were used and the entire catholyte was filtered before introduction into the cell.

after the current was shut off in order to utilize any residual amalgam.

At the conclusion of the electrolysis, the porous cups were removed, rinsed, and any precipitate collected thereon scraped off and returned to the catho-

TABLE Ia. *Effect of stirring upon yields of standard (Tesh-Lowy) method*
3 amp for 1 hr 55 min

| Expt. No. | Stirrer | Speed | Volts average | Material balance, grams | | | Yield % of theo. | Current efficiency | Conversion |
|-----------|---------|-----------|---------------|-------------------------|-----------|-----|------------------|--------------------|------------|
| | | | | Sal. ald. | Sal. acid | Tar | | | |
| 3 | 1 | mod. high | 15.0 | 4.0 | 2.0 | 2.0 | 37.7 | 30.5 | 32.3 |
| 8* | 1 | mod. high | 13.5 | 4.6 | 1.5 | 3.0 | 41.7 | 35.1 | 37.2 |
| 9 | 1 | mod. high | 13.5 | 4.5 | 1.5 | 3.0 | 40.8 | 34.4 | 36.4 |
| 10 | 2 | mod. high | 15.5 | 3.7 | 0 | 3.0 | 29.9 | 28.2 | 29.9 |
| 11 | 3 | 60 rpm | 12.5 | 4.6 | 5.0 | 0.5 | 57.9 | 35.1 | 37.2 |
| 13* | 3 | 60 rpm | 14.0 | 4.6 | 2.8 | 0.5 | 46.5 | 35.1 | 37.2 |
| 14† | 3 | 60 rpm | 12.5 | 4.7 | 1.5 | 3.5 | 42.6 | 35.9 | 38.0 |
| 16† | 3 | 250 rpm | 15.0 | 6.1 | 0 | 0.7 | 49.3 | 46.5 | 49.3 |
| 17† | 3 | 400 rpm | 14.0 | 1.8 | 6.9 | 2.1 | 28.7 | 13.7 | 14.5 |

* Fresh triple distilled Hg used.

† Quantity of Hg reduced to 25 cm³ and 3/16 in. (4.7 mm) depth.

Stirrer No. 1—Bent glass rod located off center of cell.

Stirrer No. 2—Propeller type 1 in. (2.5 cm) diameter located off center of cell.

Stirrer No. 3—Glass rod spider with 6 spokes 2.6 in. (6.5 cm) diameter located at center of cell beneath anode cups.

TABLE Ib. *Comparison of steam distillation and ether extraction procedures for recovery of salicylaldehyde from reaction mixture*

| | | | | | | | | |
|----|------------------|------|-----|-----|-----|------|------|------|
| 18 | Steam dist'n. | 12.5 | 5.0 | 1.3 | 2.5 | 44.6 | 38.2 | 40.4 |
| 19 | Ether extraction | 12.5 | 4.4 | 2.2 | 1.4 | 42.2 | 33.6 | 35.6 |

TABLE Ic. *Effect of current density upon yield*

| Expt. No. | Current density | Time | Volts average | Material balance, grams | | | Yield % of theo. | Current efficiency | Conversion |
|-----------|-----------------------|-------------|---------------|-------------------------|-----------|-----|------------------|--------------------|------------|
| | | | | Sal. ald. | Sal. acid | Tar | | | |
| 21 | 4 amp/dm ² | 2 hr 52 min | 11 | 4.5 | 4.0 | 2.0 | 51.0 | 34.4 | 36.4 |
| 23 | 7 amp/dm ² | 1 hr 39 min | 13.5 | 5.8 | 1.0 | 1.5 | 50.5 | 44.3 | 46.8 |
| 25 | 8 amp/dm ² | 1 hr 26 min | 15.0 | 6.0 | 1.0 | 2.0 | 52.3 | 45.8 | 48.5 |

TABLE Id. *Effect of intermittent electrolysis—interrupted current*

| | | | | | | | | |
|----|----------------|------|-----|-----|-----|------|------|------|
| 27 | 54 cycles/min | 13.0 | 2.3 | 6.5 | 2.0 | 34.7 | 35.1 | 18.6 |
| 28 | 108 cycles/min | 14.5 | 2.8 | 4.5 | 1.9 | 33.4 | 42.7 | 22.6 |
| 29 | 216 cycles/min | 13.0 | 2.6 | 5.0 | 2.0 | 32.7 | 39.7 | 21.0 |

TABLE Ie. *Effect of time upon yield*

| Expt. No. | Time | Stirring rate | Volts average | Sal. ald. | Sal. acid | Tar | Yield % of theo. | Current efficiency | Conversion |
|-----------|-------------|---------------|---------------|-----------|-----------|-----|------------------|--------------------|------------|
| | 32 | 1 hr | | | | | | | |
| 33 | 55 min | 250 rpm | 14.0 | 2.9 | 4.5 | 1.0 | 34.6 | 46.2 | 23.4 |
| 34 | 3 hr 50 min | 250 rpm | 12.0 | 6.3 | 0 | 2.5 | 51.0 | 24.0 | 51.0 |

After assembling the cell and cooling the contents to 15°–18°C, electrolysis was conducted at 3 amperes for 115 minutes as specified by Tesh and Lowy. Stirring of the solution was continued for 30 minutes

lyte solution which was separated from the mercury by means of a separatory funnel. The mercury was washed with two 50 ml portions of distilled water and the washings added to the catholyte mixture,

to which was also added 20 ml of concentrated sulfuric acid diluted to 100 ml with distilled water.

tained was made and this value was converted to a weight basis by applying a density factor of 1.15 grams/ml. The residue from the steam distillation

TABLE If. Influence of NaHSO_3 addition rates and concentration in catholyte upon yield

| Expt. No. | Conditions | Volts average | Material balance, grams | | | Yield % of theo. | Current efficiency | Conversion |
|-----------|---|---------------|-------------------------|-----------|-----|------------------|--------------------|------------|
| | | | Sal. ald. | Sal. acid | Tar | | | |
| 35 | 20 g NaHSO_3 added at beginning of electrolysis* | 11.0 | 3.1 | 5.2 | 2.0 | 39.9 | 23.7 | 25.0 |
| 36 | 20 g NaHSO_3 and 10 g H_3BO_3 at start; 5 g H_3BO_3 after 1 hr* | 12.0 | 3.5 | 3.9 | 2.2 | 39.2 | 26.7 | 28.2 |
| 37 | 20 g NaHSO_3 and 7.5 g H_3BO_3 at start; 7.5 g H_3BO_3 after 45 min* | 12.5 | 3.2 | 5.0 | 2.5 | 40.2 | 24.4 | 25.8 |
| 38 | 5 g NaHSO_3 at start; 8 g NaHSO_3 added at uniform rate during electrolysis† | 12.0 | 5.2 | 3.0 | 1.5 | 53.5 | 39.7 | 42.0 |

* No. 1 stirrer.

† No. 3 stirrer at 250 rpm.

TABLE Ig. Dependency of yield upon relative concentrations of boric acid and sodium bisulfite

| Expt. No. | Boric acid | NaHSO_3 | Volts average | Material balance, grams | | | Yield % of theo. | Current efficiency | Conversion |
|-----------|------------|---|---------------|-------------------------|-----------|-----|------------------|--------------------|------------|
| | | | | Sal. ald. | Sal. acid | Tar | | | |
| 42 | none | 40 g | 9.5 | 0 | — | 0 | — | 0 | |
| 43 | none | 20 | 10.0 | 0 | — | 0 | — | 0 | |
| 45 | 37.2 g | (Na_2SO_3 , equiv. amt.) | 12.0 | 5.5 | — | 1.5 | 44.5 | 42.0 | |
| 46 | 6.2 | 26 | 12.0 | 2.8 | 5.3 | 1.8 | 36.5 | 21.4 | |
| 47 | 9.3 | 23.4 | 12.0 | 4.3 | 3.0 | 2.5 | 44.3 | 32.8 | |
| 48 | 12.4 | 20.8 | 12.0 | 5.4 | 1.0 | 1.1 | 47.1 | 41.2 | |
| 49 | 15.5 | 18.2 | 11.0 | 6.2 | 0 | 1.8 | 50.1 | 47.4 | |
| 50 | 18.6 | 15.6 | 12.0 | 6.0 | 0 | 1.5 | 48.5 | 45.8 | |
| 51 | 21.7 | 13 | 12.5 | 5.9 | 0 | 2.0 | 47.7 | 45.0 | |
| 52 | 24.8 | 10.4 | 13.0 | 5.5 | 0 | 2.0 | 44.5 | 42.0 | |

TABLE Ij. Electrolytic reduction of acetylsalicylic acid or aspirin

| Expt. No. | Conditions | Volts average | Material balance, grams | | | Yield % of theo. | Current efficiency | Conversion |
|-----------|---|---------------|-------------------------|------|-----|------------------|--------------------|------------|
| | | | Ald. | Acid | Tar | | | |
| 78 | 1 hr electrolysis; steam dist'n. | 11.5 | 2.2* | 8.6† | 0.3 | 47.8 | 32.2 | 18.0 |
| 79 | no boric acid | 11.5 | 0 | — | 0 | — | 0 | 0 |
| 80 | 10 g borax to catholyte | 11.5 | 3.1* | 0 | 1.3 | 25.4 | 23.6 | 25.4 |
| 81 | 18.6 g H_3BO_3 15.6 g NaHSO_3 | 11.0 | 3.0* | 4.3† | 1.2 | 35.7 | 22.9 | 24.5 |
| 82 | 10.4 g NaHSO_3 | 10.5 | 3.8* | 0 | 1.5 | 31.1 | 29.0 | 31.1 |
| 83 | 10.4 g NaHSO_3 ; catholyte sat'd. with SO_2 to ppt. acetylsalicylic acid; filtrate acidified and extracted with ether | 12.5 | 2.9 | 5.0 | — | 24.5 | 16.5 | 17.6 |

* Salicylaldehyde.

† Salicylic acid.

The acidified mixture was then steam distilled until no further oil came over. Oil and distillate were separated and the distillate subjected to repeated steam distillations until no further oil could be obtained. A volumetric measurement of all the oil ob-

was allowed to cool and was later filtered to recover any salicylic acid and to determine the quantity of tar.

Although the above procedure applies specifically to the standard experiment, which is designated

throughout this work as the standard procedure or Tesh-Lowry method, it applies in a general way to all the experiments conducted. Any deviations from this procedure are indicated in Table I.

DISCUSSION

Table I summarizes the results and experimental conditions of the present investigation.

It will be noted that columns are included for percentage yield, current efficiency, and percentage conversion. These quantities are closely related and in many instances may be numerically identical. The percentage conversion is defined here to be the percentage of starting material converted to salicylaldehyde (or acetylsalicylaldehyde), whereas yield is calculated on the basis of aldehyde obtained as compared to the net quantity of acid used. The current efficiency would normally be (for 0.1 mole quantities) numerically identical to the percentage conversion except for the fact that, in accordance with the specifications of Tesh and Lowry, a slightly longer than theoretical time interval for electrolysis was used. Also, in calculating yield, Tesh and Lowry did not consider the quantity of acid recovered, so in general the yield figures of Tesh and Lowry correspond to percentage conversion as presented in Table I.

It was attempted in this work to account for all the material used, but in the majority of experiments it was possible to account for only about 75 per cent of the salicylic acid used. Also, the low current efficiencies cannot be readily explained. Hydrogen evolution was plainly evident in many instances, but in other cases, there appeared to be practically no evolution of hydrogen so that the low efficiency cannot be accounted for in this manner. The possibility that other unidentified materials may have been produced seems to be a plausible explanation for both low current efficiency and poor material balance.

Influence of Various Factors in the Electrolytic Reduction of Salicylic Acid to Salicylaldehyde

Although the highest yield of salicylaldehyde as reported by Tesh and Lowry was approached fairly closely, it was never quite attained. Reference to Table I will show that many results were obtained in the 35 per cent yield range; and hence, it is readily seen how certain investigators (12) concluded that 34 per cent yield was the maximum obtainable. In fact, the 55 per cent yield reported by Tesh and Lowry was included but twice and both entries in their table of results appear to be for the same experiment.

When the specifications of Tesh and Lowry are adhered to closely, the conclusion is drawn that proper stirring is of controlling importance. There appears to be for any particular stirrer an optimum speed for

best mixing the catholyte and moving fresh solution past the mercury surface without disturbing this surface. The mercury can become "poisoned" with low overvoltage elements thereby giving rise to low yield, but this source of trouble may be easily eliminated, and studies (Table Ia) in which such influences have been eliminated point to the importance of proper stirring and proper cell design.

The method employed to recover the aldehyde from the electrolyzed solution might be expected to have considerable bearing on the yield especially with respect to tar formation during steam distillation. As shown in Table Ib steam distillation suffers no disadvantage in this regard as compared to extraction procedures. Tesh and Lowry have recommended extracting the distillate with ether to recover all the available aldehyde. It was found preferable, however, to steam distill repeatedly the separated distillate both from a standpoint of convenience of operation and of total aldehyde recovery.

A study of current density (I_c) corroborated the results of Tesh and Lowry and indicated an independence of yield and current efficiency with respect to current density over a rather wide range of operation. A further attempt (I_d) to bring the rate of electrolysis into better balance with the reduction rate of the salicylic acid by the introduction of a commutator in the electrical circuit to provide an intermittent direct current gave results no different from those obtained by the usual procedure.

In order to ascertain the effect of time upon yield, several experiments (I_e) were conducted for one half the normal period of electrolysis and, in one instance, for twice the normal time. The amount of tar formed was not significantly different in any case in contradiction to what might be expected. A higher yield would be expected during the first hour of electrolysis but actually lower yields were obtained. Of more importance, but unexplained significance, is the fact that only the usual conversion of acid to aldehyde was obtained in the double length experiment along with about the usual amount of tar. Variations in the addition of sodium bisulfite (I_f) both as to rate of addition and concentration held in the catholyte also appeared to be without appreciable effect on the amount of tar formation.

The most significant findings of the present research relate to the dependence of yield upon the use and relative concentration of boric acid. Reference is made in the Weil patent (15) to the surprising observation that sodium salicylate is reduced in aqueous solution with greater ease in the presence of free boric acid. According to Mettler (9) the presence of free boric acid stops the reduction of the acid at the aldehyde in the electrolytic method when a mercury cathode is used and also in the purely

chemical method when sodium amalgam is used. Aromatic aldehydes in alkaline solution are also reported (4) to yield hydroxybenzoin derivatives. It would be concluded from this information that the chief purpose of the boric acid would be to maintain faint acidity and thus control the course or extent of reduction.

This conclusion does not appear, however, to be reasonable since the addition of excess sodium bisulfite both maintains acidity of the catholyte and stops the reduction at the aldehyde. It may be possible that a critical pH range may exist which is maintained by the buffer action of boric acid and the associated system but this does not seem too probable. It seems much more likely that the explanation

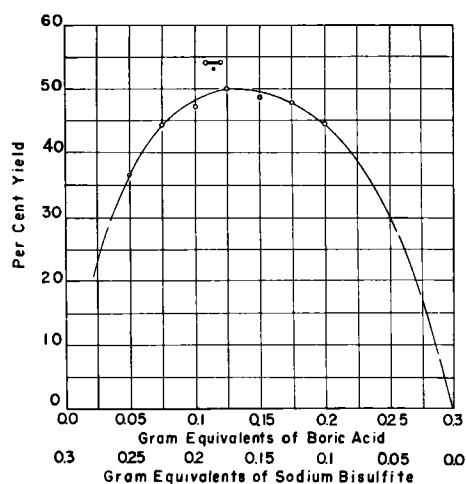


FIG. 2. Relationship of yield to relative concentrations of boric acid and sodium bisulfite. *Tesh-Low maximum yield—0.121 equivalents boric acid, 0.192 equivalents sodium bisulfite.

lies in the formation of a complex salt formed between boric acid and sodium salicylate.

Hermans (5), Meulenhoff (11), and Schafer (13) have all reported the preparation of borosalicylates and Loomis (8) was granted a patent for a process of producing salicylaldehyde by treating acid sodium borodisalicylate with sodium amalgam in the presence of sodium sulfite or bisulfite.

Table Ig shows conclusively the need for boric acid. It has also been demonstrated (Ig-45) that sodium sulfite is as effective as bisulfite in protecting the aldehyde from further reduction. This observation enabled a study of the boric acid-bisulfite relationship when the total acidity thus introduced was held equivalent to the total possible alkalinity. Fig. 2, based upon experiments Ig-46 to Ig-52, shows that an optimum relationship resulting in maximum yield exists at approximately the specifications used by Tesh and Lowy and originally set forth by Weil and Mettler.

Modifications in Apparatus Directed Toward the Design of Full Scale Equipment

Although an improvement in yield was not effected by any of the experimental conditions investigated, some thought was given to the design of commercial scale equipment. As specified by Tesh and Lowy, a considerable inventory of mercury would be indicated. It has been found that this inventory can be reduced to an absolute minimum. As a means of doing this, the mercury in the Tesh-Low apparatus was replaced in one instance by an amalgamated lead sheet and in a second instance by an amalgamated piece of sheet iron. Comparatively the amalgamated sheet iron performed much more satisfactorily than did the amalgamated lead sheet indicating the need for a continuous mercury film. The German vertical caustic cell (2), which employs the film principle, illustrates a type of construction which, with the introduction of diaphragms and certain other modifications, might possibly be advantageously adapted to the electrolytic reduction process.

A more practical approach to commercial operation would probably be to generate the sodium amalgam in a separate cell such as the German cell or the Mathieson Alkali Corporation cell (3) and to carry out the reduction step in a separate reactor. The initial attempts along this line were unsuccessful. Graphite anodes had been employed in the electrolytic cell and it is believed that the slight disintegration of these anodes furnished sufficient material to keep the amalgam concentration below a critical value. On repeating these experiments and substituting lead anodes for graphite, the results were much more satisfactory. The tower type reactor appeared to be superior to the fixed surface type in yield and is definitely so with respect to simplicity of construction. Many considerations have yet to be investigated in this regard, but it has been demonstrated at least that the method is workable and that it warrants additional effort.

The Electrolytic Reduction of Acetylsalicylic Acid

Group j of Table I summarizes the experiments performed in studying the reduction of acetylsalicylic acid to acetylsalicylaldehyde. The advantage of starting with aspirin would be, of course, the elimination of the step introducing the acetyl group into salicylaldehyde to obtain coumarin.

In general, all the observations made in the reduction of salicylaldehyde apply to the reduction of acetylsalicylaldehyde. The solubility of boric acid in the acetylsalicylic acid catholyte is not as great as for salicylic acid, but its presence is nevertheless essential to carry out any reduction.

The ease with which acetylsalicylic acid and acetylsalicylaldehyde undergo hydrolysis complicates

the study of these materials. For this reason, it was more convenient to hydrolyze the acetylsalicylaldehyde to salicylaldehyde during the steam distillation and thus to determine yields. However, to establish the synthesis of acetylsalicylaldehyde as such, the reaction mixtures were in two instances extracted with ether after first precipitating the residual acetylsalicylic acid with sulfur dioxide and then acidifying to break down any sulfite-aldehyde complex. In both cases, a material was obtained which melted between 35° and 39°C as compared to 38°–39°C as reported in Heilbron (6) for acetylsalicylaldehyde. While this by no means can be considered as identification, it would appear reasonable that acetylsalicylaldehyde was actually obtained. Regardless of positive identification the yield of acetylsalicylaldehyde is too low to be of any commercial interest, but academically, at least, the method apparently presents a new synthesis for this material.

CONCLUSION

The present investigation has substantiated the work of Tesh and Lowy on the reduction of salicylic acid to salicylaldehyde thereby disproving the limitation of the electrolytic method to the lower yields reported by other workers. The attainment of appreciably higher yields, likewise, has been shown to be improbable.

The presence of boric acid is a prime requisite in

the reduction of both salicylic and acetylsalicylic acids and the proper stirring of the catholyte is of very considerable importance.

Any discussion in this paper will appear in a Discussion Section, to be published in the December 1950 issue of the JOURNAL.

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