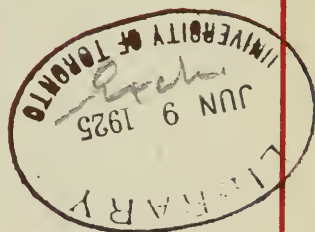


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Electrolytic Preparation of *p*-Phenylenediamine, Aminosalicylic Acid, Succinic Acid, and Hydrocinnamic Acid¹

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Details are given for the electrolytic production of *p*-phenylenediamine, aminosalicylic acid, succinic acid, and hydrocinnamic acid.

p-Phenylenediamine was prepared from *p*-nitroaniline. The yield obtained was 91.5 per cent of the theoretical, and the current efficiency 84 per cent. The cathode was carbon and the anode lead. The cathode solution was concentrated hydrochloric acid and the anode solution dilute sulfuric acid. These conditions are such that the process could be used in industrial work. In the work previously reported on the preparation of *p*-phenylenediamine platinum or nickel electrodes were used. Platinum is too expensive for industrial use and nickel is slowly disintegrated during the electrolysis.

Aminosalicylic acid was prepared by the electrolytic reduction of the compound formed by coupling benzene-diazonium chloride with salicylic acid. It was found that titanium tetrachloride served as a useful catalytic agent. The best results were obtained, however, by reducing the azo compound with titanium trichloride. A process was worked out for the electrolytic regeneration of the titanium trichloride. The combination of the two processes gave excellent results.² The yield of aminosalicylic acid was 94 per cent of the theoretical. For the regeneration of the titanium chloride the current used was practically that theoretically required.

The preparation of succinic acid by the electrolytic reduction of fumaric acid yielded 85.2 per cent of theoretical amount with a current efficiency of 77 per cent. Using maleic acid instead of fumaric the yield and current efficiency were 90.5 and 82 per cent, respectively. In the case

¹ Received October 1, 1924.

² An application for patents to cover this process has been filed.

of fumaric acid no diaphragm was necessary—a fact of considerable importance in the use of the method on the large scale.

The electrolytic reduction of cinnamic acid gave 91 per cent of the theoretical yield of hydrocinnamic acid and the current efficiency was 83 per cent.

ON ACCOUNT of the technical importance of *p*-phenylenediamine and aminosalicyclic acid, the preparation of these compounds electrolytically has been studied in detail to determine if methods could be worked out that could be applied in large-scale production. In the preparation of the latter compound titanium tetrachloride was found to be a useful catalytic agent. The best results were obtained by effecting the reduction with titanium trichloride prepared by the electrolytic reduction of the tetrachloride. Inasmuch as a process has been worked out for the electrolytic regeneration of the trichloride, its use for this purpose involves only small mechanical loss. The preparation of large quantities of titanium tetrachloride during the recent war showed that it could be made commercially available at a reasonable cost. It may therefore find an important place in the industry.

The fact that maleic and fumaric acids can be made on the large scale at a reasonable price led the writers to study the electrolytic reduction of these acids to succinic acid, which would no doubt find applications if it could be prepared at a low cost. In connection with a general study of the reduction of the ethylene linking in organic compounds the electrolytic reduction of cinnamic acid has also been investigated.

Experimental

Apparatus

A 2-liter beaker served as one compartment and a porous cup (8.5×19 cm.) as the other. The beaker was lined with a sheet lead electrode (12×15 cm.). The second electrode, which varied in the several experiments, was placed in the cup. In some of the experiments it was perforated, because with an electrode of this type better mixing of the solution is obtained and it is possible to use a higher current density without the evolution of hydrogen. In series with the electrodes were placed an ammeter shunt and a variable resistance. A voltmeter was connected across the terminals. When studying reductions the cathode was placed inside the cup.

Preparation of *p*-Phenylenediamine

A number of electrolytic methods for the preparation of this compound have been described, but none of them appears to be satisfactory on the large scale. For industrial purposes the amine is probably made by the reduction of *p*-nitroaniline by means of iron and dilute hydrochloric acid. The product made in this way is difficult to purify. *p*-Phe-

nylenediamine was first prepared electrolytically by Noyes and Dorrance,³ who used platinum electrodes and concentrated sulfuric acid solutions. Later Elbs⁴ and Kopp reduced the amine in alcoholic solution, using a nickel gauze as cathode and an anode of platinum. A process for the reduction of nitroaniline was patented in 1900;⁵ the amine was suspended in dilute hydrochloric acid and reduced at a spongy tin electrode. As far as the writers know, no electrolytic process for the preparation of *p*-phenylenediamine has been technically successful.

In an endeavor to improve and simplify the method of reduction of *p*-nitroaniline to *p*-phenylenediamine, a number of experiments were carried out using, in turn, nickel, lead, and carbon cathodes. The conditions finally found which gave very satisfactory results were as follows: Cathode, carbon plates (area 218 sq. cm.); cathode solution, 207 cc. concentrated hydrochloric acid, 293 cc. water, and 60 grams pure *p*-nitroaniline; cathode current density, 11.2 amperes per sq. dm. until 90.9 per cent of the theoretical current had passed, 5.7 amperes per sq. dm. until 1.5 per cent excess of the theoretical current had passed, and then 2.9 amperes per sq. dm. until the excess was 8.7 per cent; anode, sheet lead (12 × 15 cm.); anode solution, 5 per cent sulfuric acid; voltage across the cell, 3.8; total time for reduction, 4 hours; temperature, about 73° C.

The cathode solution was cooled and saturated with hydrogen chloride, which caused the precipitation of *p*-phenylenediamine hydrochloride. The latter was separated by filtration and dried overnight at about 65° C. on a porous plate. The yield of the product, which was shown by analysis to be 98.8 per cent pure, was 91.5 per cent of the theoretical; the current efficiency was 84 per cent. The salt was readily purified by dissolving it in a small amount of water, boiling the solution with bone black, and, after filtration, saturating the filtrate with hydrogen chloride.

In an experiment carried out as described above except that 20 cc. of a solution of titanium tetrachloride were added to the cathode solution, the yield of the product was 94.7 per cent and the current efficiency was 92.5 per cent.

Preparation of Aminosalicyclic Acid

As this compound is used in making a number of dyes, its preparation was studied. It has been made from nitrosalicyclic acid,⁶ and by the reduction by zinc dust⁷ or the electric current⁸ of dinitrobenzoic acid dissolved in concentrated sulfuric

³ *Ber.*, **28**, 2349 (1895).

⁴ *Z. Elektrochem.*, **5**, 108 (1898).

⁵ U. S. Patent 121,835 (1900).

⁶ Beilstein, *Ann.*, **130**, 243 (1864); Hubner, *Ibid.*, **195**, 18 (1879); Hirsch, *Ber.*, **33**, 3239 (1900); Denninger, *J. prakt. Chem.*, **42**, 550 (1890).

⁷ Farbwerke vorm. Meister, Lucius & Brüning, German Patent 96,853.

⁸ Catterman, *Ber.*, **26**, 1850 (1893); Farbenfabriken vorm. F. Bayer & Co., German Patent 77,806.

acid. The best method of preparation, according to Cain, is the reduction of benzeneazosalicylic acid⁹ by means of stannous chloride or sodium hyposulfite. On account of the ease of preparation of benzeneazosalicylic acid, this compound was prepared in the usual way from salicylic acid and benzenediazonium chloride, and was used in the preparation of aminosalicic acid. The direct reduction of the azo compound in alkaline solution, or in suspension in hydrochloric acid, gave unsatisfactory results. As its reduction by titanium trichloride took place smoothly, the use of this reagent and the electrolytic regeneration of the latter were studied. The results were satisfactory. The solution of titanium trichloride for the reduction was prepared as follows: To 600 cc. of concentrated hydrochloric acid were added slowly 150 cc. of titanium tetrachloride. The solution was placed in the porous cup of the cell described above. Three carbon plates served as cathode. The anodic solution was 5 per cent sulfuric acid. The reduction was effected at 60° to 70° C., with the current density 14.5 amperes per sq. dm. and a voltage drop across the cell of 3.3 volts, until 65 per cent of the chloride had been reduced. At this point the current density was reduced to 5.5 amperes per sq. dm. to prevent loss of hydrogen. During the reduction the cathodic solution was slowly stirred. The current efficiency was practically 100 per cent.

The solution of titanium trichloride prepared in this way was used to reduce benzeneazosalicylic acid. To 525 cc. of the solution were added 70 grams of the finely ground azo compound, the theoretical amount being 73.5 grams. After stirring for a few minutes the mixture was allowed to stand 26 hours. An analysis showed that 91.6 per cent of the azo compound had been reduced. The mixture was again stirred and allowed to stand 12 hours. The percentage of the compound reduced increased to 93.3.

The solid material was filtered off through asbestos and the filtrate reserved for future use. The solid was stirred with enough cold water to dissolve the aniline hydrochloride formed. The yield of the hydrochloride of aminosalicic acid obtained after this treatment with water, in which the compound is appreciably soluble, was 42 grams, or 77 per cent of the theoretical, and the salt was shown by analysis to be 98 per cent pure. To the filtrate, which contained the titanium tetrachloride and the dissolved hydrochloride of aminosalicic acid, was added a small amount of water in order to have practically the same concentration of acid as that used in the reduction of the chloride. The solution was saturated with hydrogen chloride and reduced in the manner described above. The amount of titanium tetrachloride recovered was 95.5 per cent of that originally used. This solution, which contained the hydrochlorides of aminosalicic acid and the aniline not recovered by filtration, was used to reduce more of the azo compound. To 345 cc. of the

⁹ Rosenberg, *Ber.*, **32**, 81 (1899).

solution were added 60 grams of the azo compound. The mixture was heated to 98° C., stirred for 2 hours, and allowed to stand overnight. An analysis showed that 99.6 per cent of the azo compound had been reduced. The solid was filtered off, washed with cold water to remove aniline hydrochloride, and dried in the air. The yield of the hydrochloride of aminosalicic acid obtained was 94 per cent of the theoretical. The increased yield in this case was due to the fact that the solution of titanium tetrachloride used was saturated with the hydrochloride formed in the previous reduction. The chloride was shown by analysis to be 98 per cent pure.

The recovered solutions of aniline hydrochloride could be used in preparing the azo compound from salicylic acid. This process of making the hydrochloride of aminosalicic acid involves the use of salicylic acid, hydrochloric and nitrous acids for the diazo reaction, and the small amounts of aniline and titanium tetrachloride needed to make up for the loss of these reagents.

Preparation of Succinic Acid from Maleic and Fumaric Acids

In a study of the electrolysis of concentrated solutions of the sodium salts of maleic and fumaric acids, Kekulé¹⁰ obtained acetylene and carbon dioxide at the anode. He was of the opinion that a trace of succinic acid was formed at the cathode but no experimental details as to the identification of the acid are given. Fokin¹¹ reduced fumaric acid, and later Pomilio,¹² in the study of the reduction of a number of unsaturated acids, reduced maleic and fumaric acids using a nickel gauze cathode and a platinum anode. These investigators did not report the yield of succinic acid obtained, and evidently did not have the production of this acid as their object.

The reduction of fumaric acid in alkaline and in acid solution under a variety of conditions was studied. It was found that the reduction could be effected equally well with or without a diaphragm.¹³ The most practical conditions found were as follows: The cathode, which was a perforated lead cylinder and had an area of 153 sq. cm., was placed in the center of a beaker. The anode of sheet lead, lining the inside of the beaker, had an area of 330 sq. cm. The electrolyte was prepared by adding to 900 cc. of hot water 58 grams of fumaric acid, and then a warm solution of 27 grams of concentrated sulfuric acid in 100 cc. of water. The mixture was stirred during the electrolysis until the suspended acid had dissolved. The reduction was carried out at about 84° C. and with a voltage across the cell of approximately 3 volts. The cathodic current density was 6.5 amperes per sq. dm. until about 87 per cent of the theoretical current had passed; it was then reduced to 2.5 amperes per sq. dm. until about 10

¹⁰ *Ann.*, **131**, 85 (1864).

¹¹ *Z. Elektrochem.*, **12**, 749 (1906).

¹² *Ibid.*, **21**, 444 (1915).

¹³ U. S. Patent 1,457,791 (1923) covers this process.

per cent excess of current had been used. The solution was filtered, evaporated to about 100 cc., and allowed to cool. The crystals were separated and the filtrate was evaporated to 70 cc. The two crops of crystals obtained gave a yield of 85.2 per cent of the theoretical amount, which corresponds to a current efficiency of 77 per cent. The melting point of the succinic acid, without further purification, was 179° to 180° C.

The experiments with maleic acid showed that a diaphragm was necessary. The best result was obtained by the following procedure: The cathode was a sheet lead cylinder (area 189 sq. cm.) which was placed in a porous cup. The anode was sheet lead which lined a beaker. The cathodic solution was a mixture of 28.4 concentrated sulfuric acid and 400 cc. water to which 116 grams of maleic acid were added. The anodic solution was 5 per cent sulfuric acid. During the electrolysis the current density at the cathode was 7.7 amperes per sq. dm. until 96.3 per cent of the theoretical current had passed. It was then reduced to 3.1 amperes per sq. dm. until 4.4 per cent excess of current had passed. The current efficiency was 82 per cent.

The cathodic solution was filtered, evaporated to 70 cc., and cooled in ice water. The yield of succinic acid, which melted at 179° to 181° C., was 90.5 per cent of the theoretical.

Preparation of Hydrocinnamic Acid

Marie¹⁴ prepared this acid by the electrolytic reduction of cinnamic acid. He used a mercury cathode, which presented some difficulties.

The first experiments showed that an appreciable amount of sodium cinnamate was transferred to the anodic compartment when the salt was electrolyzed. To avoid this the reduction was carried out in the presence of an excess of sodium hydroxide. The best conditions found were as follows: Cathode sheet lead (area 260 sq. cm.); anode, sheet lead. The cathodic solution was prepared by adding 30 grams of cinnamic acid to a warm solution of 8.1 grams of sodium hydroxide dissolved in 400 cc. water. The solution was transferred to a porous cup, heated to about 50° C., and stirred rapidly. A solution of 25 grams of sodium hydroxide in 100 cc. of warm water was then slowly added. The addition of the excess of alkali caused the precipitation of a part of the sodium cinnamate. The solution was stirred during the electrolysis until the suspended matter dissolved. The temperature was kept at about 60° C. A current density of 5.7 amperes per sq. dm. was maintained until 90.7 per cent of the theoretical current had passed; it was then reduced to 2.4 amperes per sq. dm. until 9.8 per cent excess had passed. The current efficiency therefore was 83 per cent.

The cathodic solution was cooled in ice water, and a large excess of concentrated hydrochloric acid was added. An oil

¹⁴ *Compt. rend.*, **136**, 1331 (1903).

separated, which was filtered off after it had solidified. The hydrocinnamic acid melted at 46.7° to 48° C. The yield was 91 per cent of the theoretical.

