Electrolytic Reduction of Maleimide and Pyrroline.

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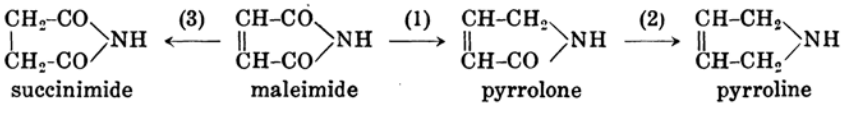
In his recent researches on the electrolytic reduction of succinimide(1) and its derivatives, the present writer observed the remarkable reducing power of zinc amalgam which, when used as the cathode in a strong sulphuric acid solution, could well reduce both carbonyl groups into methylene.

In the electrolysis of pyrrol(2), however, conjugate double bonds were found not to be reduced by zinc amalgam, while the same reduction could easily be brought about by an addition of nickel. With the object of confirming whether such different behaviours of carbonyls and unsaturated carbon atoms towards the cathode are also observable in the radicals contained in a molecule, the electrolytic reduction of maleimide has been attempted.

If the above holds good, maleimide should be reduced in either one of the following ways according to the kind of cathode:



That is to say, if zinc amalgam is used as cathode, pyrroline will be obtained according to (1) and (2) and if reduced nickel is used instead, succinimide must be produced according to (3).

As the result of the experiments it was found that the reaction (3) took place quite smoothly, proceeding quantitatively at lead or copper cathode in dilute sulphuric acid solution, in which reduced nickel was suspended. With

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(1) This Bulletin, **10** (1935), 311; **11** (1936), 41.

(2) This Bulletin, **11** (1936), 374.

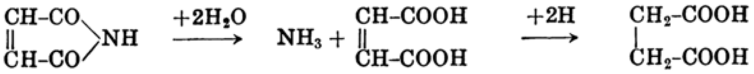
zinc amalgam cathode, however, no such reaction could be observed, the material having been decomposed into succinic acid and ammonia. For the problem how succinic acid was produced in the above electrolysis two solutions are conceivable:

(1) First maleimide is reduced to succinimide and then decomposed into succinic acid and ammonia in alkaline electrolyte.

(2) Maleimide is first decomposed into maleic acid and ammonia and maleic acid thus produced is then reduced to succinic acid.

If solution (1) be right, pyrrolidone and pyrrolidine must have been produced from succinimide according to the result previously obtained by the present writer. This is, however, contrary to the facts.

Thus solution (2) may be regarded as the more probable, that is, may be taken to occur according to the following scheme:



$$\begin{array}{l} CH-CO \\ \| \\ CH-CO \end{array}\!\!>NH \xrightarrow{+2H_2O} NH_3 + \begin{array}{l} CH-COOH \\ \| \\ CH-COOH \end{array} \xrightarrow{+2H} \begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$$

As the decomposition was considered to be dependent upon the concentration of sulphuric acid, experiments were repeated with 10% as well as with 30% sulphuric acid. But in no case reduction of carbonyl groups was attained.

Experimental.

Maleimide(3) was prepared by oxidising pyrrol with potassium bichromate and sulphuric acid, and obtained as sublimable brown crystals melting at 93°.

Pyrroline(4) was prepared by reducing pyrrol with zinc dust and hydrochloric acid. It was a colourless liquid with ammonia smell, boiling at 90°.

Nickel catalyser was prepared from nickel hydroxide precipitated by carefully adding a sodium hydroxide solution to nickel sulphate solution, which was first ignited and then reduced at a temperature between 320° and 330° in pure hydrogen gas.

Zinc amalgam electrode was the same that was used in the electrolysis of succinimide.

I. **Reduction of Maleimide with Reduced Nickel.** The electrolysis was undertaken under the conditions as follows: Cathode: lead tube (50 sq. cm.). Catholyte: 100 c.c. of 10% sulphuric acid and 2 g. of maleimide and 0.5 g. of reduced nickel. Anode: lead plate. Anolyte: 10% sulphuric acid. Current density: 12 amp per 100 sq. cm. Current quantity: 38.0 F per mol. Temperature: 28°.

The imide dissolved gradually in the catholyte giving a yellow solution. From time to time the nickel catalyser in the form of finest dust was added to the catholyte. The catholyte and anolyte were separated by a cylindrical vessel of biscuit, and through the cathode tube a rapid current of water was made to pass. Thus the apparatus was well cooled with water from inside and outside and the cathodic solution was stirred vigorously throughout the electrolysis. After 3.5 hours' electrolysis, the catalyser was filtered off

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(3) G. Plaucher and F. Cattadori, *Atti. accad. Lincei*, (5), **13** (1904), 489.

(4) Knorr, *Ber.* **34** (1907), 3497.

from the cathodic solution. Extracting the filtrate with ether several times 1.8 g. of colourless amorphous crystals were obtained. Recrystallized from alcohol, the substance melted at 125° alone and in admixture with succinimide. Thus, the reduction product was inferred to be succinimide.

The green mother liquid was made alkaline with caustic soda, and extracted with ether. But no basic substance was obtained. This experiment shows, therefore, that succinimide was the only reduction product in the electrolysis. With copper electrode succinimide was also obtained with a yield of 80%.

II. **Reduction of Maleimide with Zinc Amalgam.** The conditions of the electrolysis were as follows: Cathode: zinc amalgam (15.8 sq. cm.). Cathodic solution: mixture of 100 c.c. of 50% sulphuric acid, 10 c.c. of alcohol, and 2 g. of maleimide. Anode: lead plate. Anodic solution: 50% sulphuric acid solution. Current density: 113.5 amp per 100 sq. cm. Current quantity: 195.8 F per mol. Temperature: 30°.

During the electrolysis, the solution was prevented from foaming by adding a small portion of alcohol, and to prevent the rise of temperature a spiral lead tube, through which cold water was rapidly running, was inserted into the catholyte. The apparatus was kept cool in water, and the catholyte was stirred vigorously throughout the electrolysis. The yellow colour of the catholyte gradually faded away as the electrolysis went on. After 6 hours the electrolysis was stopped, and the colourless cathodic solution was extracted with ether. On evaporating ether about 1.2 g. of colourless substance was obtained. When recrystallized from alcohol, this substance became prismatic crystals, which melted at 183° alone and in admixture with succinic acid. The substance, therefore, undoubtedly was succinic acid. The mother liquer, when made alkaline with a sodium hydroxide solution, emitted a distinct smell of ammonia. It was therefore subjected to steam distillation, and the distillate was acidified with hydrochloric acid, and evaporated to dryness, whereupon a colourless crystalline salt weighing about one gram was produced. The gold double salt of it did not melt at a temperature higher than 250°. Found: Au, 54.55. Calculated for $NH_4Cl \cdot AuCl_3$: Au, 55.18%. This shows that the substance was nothing but ammonium chloride, containing neither pyrrolidone nor pyrrolidine. Two more electrolyses were repeated with 10 and with 30% sulphuric acid with different results.

III. **Reduction of Maleic Acid.** As a subsidiary means of finding the cause of the production of succinic acid in the preceding experiment, maleic acid was electrolysed under the same conditions. From 2 g. of maleic acid, 1.8 g. of prismatic crystals were produced in 4 hours' electrolysis (current quantity: 130.3 F per mol). The crystals melted at 183°, the melting point of succinic acid. The yield was 83% of the theoretical.

IV. **Reduction of Pyrroline.** The electrolysis was carried out under the following conditions: Cathode: lead tube of 50 sq. cm. Cathodic solution: 2 g. of pyrroline dissolved in 100 c.c. of 10% sulphuric acid to which about 0.5 g. of reduced nickel was added from time to time. Anode: lead plate. Anodic solution: 10% sulphuric acid solution. Current density: 7 amp. per 100 sq. cm. Current quantity: 10.3 F per mol. Temperature: 29°. The electrolysis was conducted in the same manner as in I.

When the electrolysis was over, the greenish cathodic solution was taken out and made alkaline with a sodium hydroxide solution, when a strong ammonia-like smell was evolved. The solution was then subjected to steam distillation, and the distillate was evaporated after having been acidified with hydrochloric acid. Colourless needles weighing 1.5 g. were obtained. The auric double salt was produced as yellow needles, melting at 203° with partial decomposition. Found: Au, 47.89. Calculated for $C_4H_9N \cdot HCl \cdot AuCl_3$: Au, 47.95%. It is beyond doubt that the substance was the gold salt of pyrrolidine.

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