ELECTROLYTIC REDUCTION OF SUCCINIMIDE.

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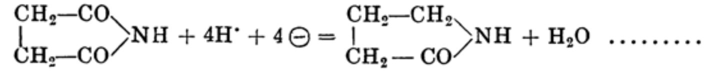
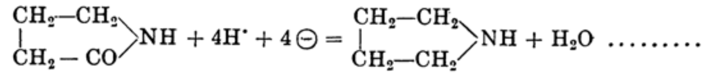
When succinimide is subjected to reduction, it is supposed, in the first stage one of its carbonyl groups undergoes reduction giving rise to the formation of pyrrolidone, and then, by further strong reduction, the other carbonyl group is reduced, pyrrolidine being produced as the complete reduction product:



$$\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\!\!>NH + 4H^{\cdot} + 4\ominus = \begin{array}{l}CH_2-CH_2\\ |\\ CH_2-CO\end{array}\!\!>NH + H_2O \;\ldots\ldots\ldots\; (1),$$

Succinimide Pyrrolidone



$$\begin{array}{l}CH_2-CH_2\\ |\\ CH_2-CO\end{array}\!\!>NH + 4H^{\cdot} + 4\ominus = \begin{array}{l}CH_2-CH_2\\ |\\ CH_2-CH_2\end{array}\!\!>NH + H_2O \;\ldots\ldots\ldots\; (2).$$

Pyrrolidine

Many researches have already been reported on the reduction of succinimide, both chemical and electrolytical, with a view to obtain pyrrolidine.

For instance, A. Ladenberg(1) reduced succinimide chemically with metallic sodium in a solution of pure ethyl alcohol, and obtained a small quantity of pyrrolidine. J. Schnick(2) used amyl alcohol in place of ethyl alcohol with a little increase in the yield of pyrrolidine.

J. Tafel(3) attempted an electrolytic reduction with lead cathode of strong reducing ability in solution of 50% sulphuric acid and with very high current density, and obtained pyrrolidone, the product formed by the reduction of only one of the two carbonyl groups. E. Späth(4) also tried a similar electrolysis with derivatives of succinimide and obtained a fair yield of reduction products corresponding to pyrrolidine. Thus the reduction of succinimide itself has been considered more difficult than that of its derivatives.

As the present writer previously recognized the stronger reducing power in zinc amalgam cathode than in lead cathode, he applied it to the projected reduction of succinimide and succeeded in obtaining a pretty good result with a greater yield than in any foregoing experiments.

The cathode for the reduction of such a difficultly reducible substance must be made with an extremely pure material in order to acquire a high reducing power, and, therefore, metals with impurities and consequently with lower overvoltage must not be used. The cathode of zinc amalgam used was made as pure as possible in the following manner. An unglazed cylindrical cell 5 cm. in diametre and 15 cm. in height, which had been prepared with special care as to material, was treated with hot dilute hydrochloric acid for several days until it had no colour. Thus all impurities were dissolved away. Then 250 g. of redistilled pure mercury from E. Merck was introduced into the cylinder and a saturated aqueous solution of pure zinc sulphate also from E. Merck was poured on it. This cell was put in a glass vessel containing pure dilute sulphuric acid and a lead electrode. Zinc was produced by electrolysis on the surface of the mercury as cathode and the lead as anode. When the electrolysis went far enough and the mercury solidified into a sponge-like substance, it was stopped. Zinc amalgam thus prepared was used in the experiments.

The conditions of electrolysis were as follows: Cathode, zinc amalgam, 15 sq. cm.; cathodic solution, 100 c.c. of 50% H_2SO_4 from E. Merck; anode, cylindrical lead; anodic solution, pure 50% H_2SO_4; current density, 100 amperes for 100 sq. cm.; temperature, 38°–40°; time of electrolysis, 6 hours.

Succinimide (10 g.) was introduced into the cathodic solution and the solution was electrolysed with vigorous agitation. The cathodic solution was

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(1) *Ber.*, **20** (1887), 2215.

(2) *Ber.*, **32** (1899), 952.

(3) *Ber.*, **33** (1900), 2224; *Z. physik. Chem.*, **35** (1905), 433.

(4) *Mona sh.*, **50** (1928), 349.

cooled during electrolysis by passing cold water through a lead tube inserted in the porcelain cylinder, and the vessel was placed in circulating cold water. The imide dissolved after a little while into a transparent solution. For about half an hour from the beginning the evolution of hydrogen gas was very slight, indicating a smooth reduction. Then the evolution of hydrogen gas increased gradually. When the electrolysis was over, the cathodic solution was taken out and made weakly alkaline with caustic soda solution under cooling in cold water. The characteristic odour of pyrrolidine, the complete reduction product, was set free, and red litmus paper brought near turned blue at once, indicating the presence of a volatile base.

Then the solution was subjected to steam distillation and pyrrolidine distilled off easily with steam. The distillation was continued until red litmus paper changed its colour no more. As pyrrolidine is easily soluble in water, the distillate was a dilute aqueous solution of it. After neutralization of this solution with hydrochloric acid and evaporation on a water bath there remained 1.5 g. of the hydrochloride of pyrrolidine, which corresponded to 14% of the theoretical yield. The gold salt of pyrrolidine which was precipitated on addition of gold chloride melted at 205°. Found: Au, 47.85. Calc. for $C_4H_9N \cdot HCl \cdot AuCl_3$; Au, 47.95%.

The residual solution in the distilling flask was precisely neutralized with sulphuric acid, and after sodium sulphate, which crystallized on cooling the solution, was removed, pyrrolidone, the partial reduction product, remained as an oily substance. It was extracted with ether and 5 g. of crude pyrrolidone was obtained after the removal of the ether. When it was distilled, pure pyrrolidone distilled over at 250°. In a cold place it became crystals melting at 25°.

When succinimide was electrolysed for 12 hours, other conditions being the same as before, the yield of pyrrolidine increased to 28%. If the electrolysis takes place at above 60° and the concentration of sulphuric acid is 50%, succinimide decomposes into succinic acid and ammonia.(5) If sulphuric acid of 65% or over be used, the decomposition happens more easily. If the sulphuric acid is 30% or under, the decomposition does not happen even at 80°, while no reduction takes place.

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(5) Pannain, *Gazz. chim. ital.*, **35**, II, 94.