ELECTROLYTIC REDUCTION OF PYRROLE.

By **Buhei** SAKURAI.

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Reduction of pyrrole which is expected to produce pyrroline or pyrrolidine according to the strength of reduction, has been undertaken by many authors⑴ both chemically and electrolytically. The results of their experiments show that the complete reduction is attainable only when some catalysers,⑵ such as reduced nickel, platinum oxide, palladium oxide or ferric chloride are used in reduction. As to the electrolytical reduction, there is a

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(1) Ciamician and Dennstedt, *Ber.*, **16** (1883), 1536; Knorr and Rabe, *Ber.*, **34** (1901), 3491; M. Padoa, *Gazz. chim. ital.*, **36**, II (1906), 317; N. J. Putochin, *Ber.*, **55B** (1922), 2742; Adams, *Chem. Zentr.*, **95** (1924), I, 281; Meta de Jong and J. P. Wibout, *Rec. trav. chim.*, **49** (1930), 237; Zelinsky and Jurjew, *Chem. Zentr.*, **100** (1929), II, 3012; *Ber.*, **64** (1931), 101.

(2) N. J. Putochin, *J. Russ. Chem. Soc.*, **62** (1930), 2216.

German patent by Dennstedt⁽³⁾ who reduced pyrrole in a dilute sulphuric acid solution with a lead cathode and a current density of 1 amp. per sq. cm. and obtained pyrroline. From the results of the researches mentioned above, it seems that the complete reduction of pyrrole is possible only when some catalyser is present, no matter whether the reduction is undertaken chemically or electrolytically.

In the experiments here reported the present writer first tried to reduce pyrrole electrolytically by using zinc amalgam as the cathode. But as it failed to reduce pyrrole completely to pyrrolidine, electrolytic reduction in the presence of reduced nickel and platinum black was next tried. The reduction was carried out in the solution consisting of the mixture of 10% sulphuric acid and alcohol in equal volume and containing the catalyser in suspension. By this process pyrrole was for the first time completely reduced to pyrrolidine which was produced in a 15.6% yield. In this reduction a cathode having high over-voltage is not necessary. Copper gives equally satisfactory results. There was no appreciable difference between nickel and platinum, and strange to say the yield of the reduction product could not be increased above a certain limit by merely increasing the time of electrolysis.

Experiments. The catalyser was prepared in the following way. Nickel sulphate repeatedly recrystallized was dissolved in water, and nickel hydroxide was precipitated from it with sodium hydroxide. The precipitate, after having been filtered and washed with water till no reaction of sulphate appeared in the filtrate, was dried, ignited, and reduced in a combustion tube through which purified hydrogen gas was caused to flow at a temperature of 320–330°. The nickel thus reduced was cooled in the hydrogen gas and kept in absolute alcohol. Platinum black was made from platinum chloride by adding potassium hydroxide solution.

The conditions of the elecrolysis were as follows. Cathode: spiral lead tube having surface area of 50 sq. cm.; cathodic solution: mixture of 50 c.c. of 10% sulphuric acid and 50 c.c. of alcohol, to which 2 g. of pyrrole and 0.2 g. of reduced nickel were added; anode: lead plate; anodic solution: 10% sulphuric acid; temperature: 30–34°; current density: 12 amp. per 100 sq. cm.; current quantity: 45 F. per mol.

Pyrrole dissolved in sulphuric acid gradually changes into an insoluble substance of reddish-brown colour on standing. This tendency increases when the density of sulphuric acid increases and the temperature rises. So electrolysis must be carried out with a dilute solution of sulphuric acid at low temperature. As sulphuric acid solution foams vigorously during electrolysis, it is convenient to add some alcohol to the electrolytic solution.

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(3) Dennstedt, D. R. P. 127086 (1901).

The whole apparatus was kept in water and through the cathode tube water was caused to flow so as to cool it both from inside and outside, while the cathodic solution was kept stirred all through the electrolysis. As the electrolysis proceeds, the smell of pyrrole decreased gradually and at last completely faded out. After six hours' electrolysis the current was cut. The cathodic solution was taken out, and filtered, and the filtrate was evaporated on the water bath in order to drive off alcohol. The solution was now made alkaline with sodium hydroxide solution, and subjected to steam distillation. The distillate smelling of ammonia was introduced into dilute hydrochloric acid solution, and evaporated to dryness, when 0.5 g. of colourless crystalline material remained as the residue. To separate pyrroline from pyrrolidine as nitrosopyrroline the residue was again dissolved in 15% hydrochloric acid, previously cooled with ice, and 25% potassium nitrate solution was added. After a day it was extracted with ether, but no trace of nitrosopyrroline was obtained. The remaining solution was again made alkaline with sodium hydroxide solution and subjected to steam distillation, and the hydrochloric acid salt of pyrrolidine was isolated from it. Its gold double salt melting at 205° was analysed with the following results: 0.1900 g. of the salt left on ignition 0.0912 g. of gold (Found: Au, 48.10. Cal. for $C_4H_{10}NAuCl_4$: Au, 47.96%).

With a copper tube cathode pyrrolidine was also obtained in nearly the same yield. Even though the electrolysis was continued two or four times longer, the yield of pyrrolidine never increased. The higher current density was unfavourable as it caused a rise of temperature.

When platinum black was used as the catalyser 0.55 g. (corresponding to 17.6%) of hydrochloric acid salt of pyrrolidine was obtained under the same conditions.

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Osaka Women's College,
Sumiyoshi, Osaka.