Electrolytic Reduction of N-Phenyl-succinimide.

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The direct reduction of *N*-phenyl-succinimide to *N*-phenyl-pyrrolidine is so difficult that no chemical method has hitherto succeeded even in reducing one of the two carbonyls. By using a lead cathode Tafel⁽¹⁾ attained it electrolytically, but still his method was not fruitful to reduce both of the carbonyls.

Phenyl derivatives are generally seen to be less reducible than corresponding methyl or ethyl derivatives. So that, in electrolytic reduction of the former the more concentrated acid and the higher temperature are required.

As the present writer⁽²⁾ had previously succeeded in completely reducing succinimide and its methyl and ethyl derivatives by using a zinc amalgam cathode, the trial was now undertaken to see whether the same method is successful to reduce *N*-phenyl-succinimide or not.

For the complete reduction of this substance far stronger reducing action seems necessary. But the use of the stronger sulphuric acid and the higher temperature are feared for destroying the reduction product, if any. Selection of the best conditions for the electrolytic reduction thus becomes very difficult. After many trials the present writer could obtain *N*-phenyl-pyrrolidine in a 30% yield by passing a current of high density, to a zinc amalgam cathode in a 50% sulphuric acid solution at a temperature of 25°.

N-phenyl-succinimide or succinanil used in the electrolysis was prepared after Menschtkin's method,⁽³⁾ by fusing a mixture of succinic acid and aniline in a retort, and purified by recrystallizing the product from alcohol. It formed colourless needles melting at 156°.

In the reduction of this substance it must be noted that a 50% sulphuric acid solution which acts most effectively upon other substances of similar constitution is also fit for reducing phenyl-pyrrolidone into phenyl-pyrrolidine, but it is unfavourable for reducing phenyl-succinimide into phenyl-pyrrolidone, and for the latter purpose a 90% sulphuric acid

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(1) Tafel, *Ber.*, **32** (1899), 74.

(2) B. Sakurai, this Bulletin, **10** (1935), 311; **11** (1936), 41.

(3) Menschtkin, *Ann.*, **162** (1873), 166.

is the most favourable. It is, therefore, not wise to employ a solution of 50% sulphuric acid from the start. It is advisable to divide the electrolysis into two stages: In the first stage the material is reduced to *N*-phenyl-pyrrolidone by passing a current of low density with a lead cathode, and in next stage the electrolysis is intensified for the completion of the reduction, using high current density, a zinc amalgam cathode and a dilute solution of 50% sulphuric acid.

The conditions of the electrolysis taken by the author are as shown in Table 1.

Table 1.

	First part of electrolysis	Second part of electrolysis
Cathode	Lead plate; 100 sq. cm. of area	Zinc amalgam; 15.8 sq. cm. of area
Catholyte	100 c.c. of 90% sulphuric acid to which 10 g. of *N*-phenyl-succinimide was added	Catholyte was diluted till H_2SO_4 becomes about 50%
Anode	Lead plate	Lead plate
Anolyte	50% sulphuric acid	50% sulphuric acid
Current density	5 amp. per 100 sq. cm.	95 amp. per 100 sq. cm.
Time of electrolysis	10 hours	24 hours
Current quantity	32.5 F. per mol	209 F. per mol
Temperature	55°	25°

In the electrolysis of the first stage, the vessel containing the catholyte was not cooled from outside. The temperature of the catholyte rose gradually up to 55° and the material wholly dissolved in the catholyte in the course of electrolysis. If all of the material is put in at a time, it makes the solution foamy owing to its small solubility. It is, therefore, convenient to add half of it at first, and waiting till all have been dissolved (some two hours are required), the other half is added to it. In 5 hours all were dissolved, but to complete the electrolysis the current was passed for another 5 hours.

Now lead cathode was replaced with zinc amalgam and the catholyte was diluted with 130 c.c. of water, and a spiral lead tube was inserted in it, through which water was passed. The vessel was kept in a tub in which cold water circulated, so as to cool the catholyte from inside and outside. The electrolyte was kept stirred vigorously, and electric current of 15 amp. was passed.

After the completion of the electrolysis a colourless liquid obtained was shaken with ether, and about 1.2 g. of needle crystals were obtained. After cooling with water, when the electrolytic solution was made alkaline with sodium hydroxide solution, dark-brown oily substance of peculiar smell appeared on the surface. By extracting it with ether 2.5 g. of oil were obtained. The first substance from the acid solution was proved to be *N*-phenyl-pyrrolidone, which, when crystallized from ether, melted at 68°.

The second substance obtained from the alkaline solution was brown nonvolatile oil having a peculiar smell, insoluble in water but easily soluble in alcohol or ether. The solution in ether showed a bright red colour. The oil is basic and gradually dissolves in a dilute acid solution. Its platinum double chloride forms yellow needles melting at 175° with decomposition. (Found: Pt, 27.8. Calculated for $(C_{10}H_{13}N)_2H_2PtCl_6$: Pt, 27.8%).

The above-mentioned properties thus far confirmed are identical with those of the *N*-phenyl-pyrrolidine(4) prepared in purely chemical manner.

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(4) Lyman C. Craig and R. M. Hixon, *J. Am. Chem. Soc.*, **52** (1930), 804.