

Electrolytic Reduction of Phthalimide and its Derivatives V.

Reduction under high Pressure*

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Introduction

In electrolytic reaction, as has already been known, whether it is reduction or oxidation the product is influenced by the kind of electrode, current density, temperature, condition of electrolyte etc. The author considers moreover the pressure is an important element in addition to them. Because in electrolytic reduction for instance, the path of hydrogen ion which is discharged at cathode is supposed to be as follows before its appearance as hydrogen gas.

- (1) Discharge of hydrogen ion $H^+ + e \rightarrow H$
- (2) Production of hydrogen molecule $H + H \rightarrow H_2$
- (3) Appearance as hydrogen gas

As hydrogen generated as bubble has no reducing faculty, the effect of the pressure must be considered to exist before the third stage of the above mentioned process is reached. On the other hand, it is not clear which of the two steps (1) or (2) is the rate determining step of overvoltage generating hydrogen gas at cathode, but it is decided that there is no relation between pressure and overvoltage.⁽¹⁾⁽²⁾

It is considered that a large number of molecules of hydrogen must collect together before the appearance of gas in (3). Consequently, the hydrogen molecules produced at (2) cannot be isolated as hydrogen gas at the very instant of its generation. The appearance of hydrogen gas is possible only after a numerous number of molecules are gathered together, in other words the concentration has become sufficiently high. Pressure is considered to be a factor to rise the density of the hydrogen molecules at the surface of cathode, and delay the production of hydrogen molecules.

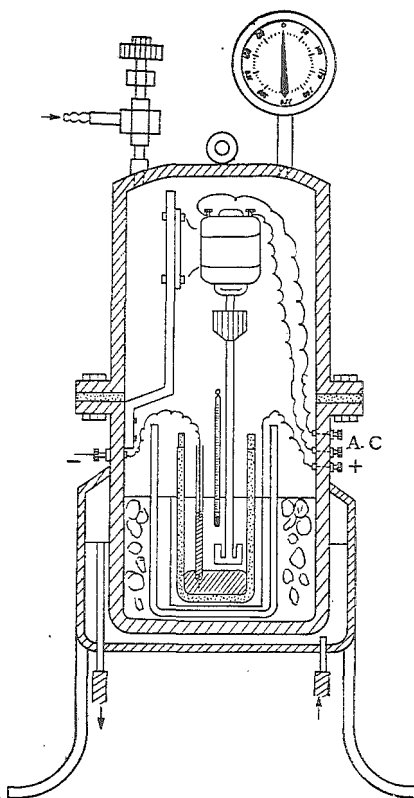
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Under the consideration mentioned above the author tried electrolytic reduction under high pressure of phthalimide and its n-methyl and n-ethyl derivatives which were electrolyzed last year, and perceived a comfortably satisfactory result, compared with the result obtained under the ordinary pressure and the same conditions. S. Ono has also applied the same method to anthraquinone etc. recently and obtaining a good result.

Experimental

Apparatus for pressure

The autoclave used for this experiment was prepared at Ito physical and Chemical Industry Ltd. by special order, the section of it is as follows.



The pressure chamber was a spherical cylinder of iron plate of 13 mm. in thickness, 30 cm. of diameter and 85 cm. of height, and it was divided in two parts, the upper and the lower. The electrolytic bath was put in the lower part, the stirrer and the necessary electric motor were held in the upper part. The two parts could be combined airtight by 16 nuts and rubber packing between them. In case of pressing, compressed air was introduced into the chamber by an air compressor for motor cars. Before the experiment the chamber had been cooled in a tub filled with pieces of ice as there were no other possible means of cooling it.

Condition of Electrolysis

As the aim of this study lay in the investigation of the effect of pressure, other conditions except electrode were strictly kept constant

as follows.

Cathode: lead plate (100 cm² of area) or zinc amalgam. (15.8 cm² of area)

Cathodic solution: mixture of 60 cc of 50% sulfuric acid and 40 cc of 90% alcohol, with 2 gms of imide added.

Anode: Lead plate of cylindrical.

Anodic solution : sulfuric acid of 50%.

Current density : 5 amp 100 cm² when lead plate is used.

13.6 amp. per 100 cm² when zinc amalgam cathode is used.

Time of electrolysis : 2.5 hours.

Cathodic solution and anodic solution were separated by an unglazed pottery cylinder, and the cathodic solution were stirred vigorously during the process of electrolysis. The electrolytic cylinder had been cooled by putting into a bath containing much ice. Consequently, the temperature of the electrolyte did not rise above 40°C. The amount of pressure applied to it were 5.3 and 8.5 atms. besides ordinary pressure for the purpose of comparison.

Treatment of Electrolyte.

Electrolytic material did not dissolve clearly at the beginning of electrolysis, but it became clear after a little while and at last turned brown after 2.5 hours'. The electrolyte was transferred into an evaporating dish and after the removal of the alcohol on a water bath, was made weakly alkaline with the aid of sodium hydroxide solution. Hereupon the perfect reduction product was isolated to the surface as oily liquid. The solution was then transferred into a flask and was digested to steam distillation, and the perfect reduction product of oily substance was distilled out together with steam. The distillation was kept on as the distillate showed alkaline, because the reduction product had indicated alkaline. Then the distillate was turned acidic by hydrochloric acid, and was evaporated to dryness over a water bath and the colorless crystal of hydrochloric acid salt of reduction product remained. As the semireduction product, one of the two carbonyls is reduced was considered be remaining in the mother liquor, it was evaporated on a water bath and condensed, extracted with ether when cooled, and recrystallized with alcohol, and colorless needle crystal was obtained.

Results

The melting points and the yield of the reduction products obtained by the above method were showed as follows.

Table

Starting material	Reduction product	Yield (%)					
		Lead cathode			Zinc amalgam cathode		
		0 (open)	5.3 atm	8.5 atm	0 (open)	5.3 atm	8.5 atm
$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{NH}$ M.P. 238°	$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagdown \text{CO} \diagup \end{array} \text{NH}$ m.p. 147°	—	—	—	33.8	28.4	36.9
	$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagdown \text{CH}_2 \diagup \end{array} \text{NH}$ HCl salt m.p. 238°	—	—	—	16.2	19.8	27.7
$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{NCH}_3$ M.P. 132°	$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagdown \text{CO} \diagup \end{array} \text{NCH}_3$ m.p. 111°	4.67	13.6	8.63	28.4	21.6	13.5
	$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagdown \text{CH}_2 \diagup \end{array} \text{NCH}_3$ HCl salt m.p. 190°	14.6	23.3	33.0	19.9	26.2	48.9
$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{NC}_2\text{H}_5$ M.P. 78°	$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagdown \text{CO} \diagup \end{array} \text{NC}_2\text{H}_5$ m.p. 101°	4.08	13.9	8.49	36.5	32.5	21.5
	$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagdown \text{CH}_2 \diagup \end{array} \text{NC}_2\text{H}_5$ HCl salt m.p. 145°	14.6	16.8	32.1	27.9	36.4	42.7

Note; Reduction of phthalimide by lead cathode was not examined.

Discussion

From the results seen above it was understood that the yield of the reduction products increased together with the increase of pressure in all cases, especially when the pressure was 8.5 atms the increase of the yield was obviously evident, and also the effect of the pressure to electrolytic reaction was clearly proved.

The decrease of the yield of semireduction products with the pressure is to be considered to indicate the increase of the quantity of the substance that entered into the perfect reduction and it does not deny the effect of the pressure. The fact that the yield by lead cathode was smaller than that by zinc amalgam verifies not only that the reducing power of zinc amalgam is stronger than that of lead cathode but that even the reduction of the primary stage can hardly exist under an ordinary pressure.

Among the three kinds of imide whose atoms or radicals are connected to the nitrogen atoms of imide, hydrogen has the least reducibility and if it is replaced by methyl group the imide changes to be easily

reducible, and when it was replaced with ethyl radical the reducibility increases more.

The author had intended to try the reduction under a still more high pressure but it was not to be accomplished by the compressor that was not fit for a higher pressure than above. If the experiment under a higher pressure could be done, the reduction would be carried out with much more facility, and it is supposed that also substance that cannot be reduced under ordinary pressure would become reducible under a higher pressure. Concerning these substances the author intends further investigations.

Summary

Phthalimide, n-methylphthalimide and n-ethylphthalimide were electrolytically reduced under high pressure, and the result obtained was compared with that obtained under the ordinary pressure.

Reduction increased together with the increase of the pressure.

Zinc amalgam cathode was effective than lead cathode.

Methyl or ethyl derivatives were more easily reducible than phthalimide.

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