THE ELECTROLYTIC REDUCTION OF PHTHALIMIDES.
PART I.

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Received May 14, 1930. Published June 28, 1930.

The electrolytic reduction of phthalimide was undertaken by T. Shimamoto, S. Araki and M. Hanawa at suggestion of Professor M. Matsui in his laboratory, but they could not continue the work to completion. I, therefore, took up the problem as a part of a general theme dealing with the electrolytic reduction of cyclic imides and tried to make the progress of the reaction clear, freely consulting the results obtained by the above mentioned colleagues.

So far as my experiments were concerned the electrolytic reduction was observed to proceed only to the stage of pyrrolidone, the further reduction to the pyrrol or the pyrrolidine stage having been unattainable in all cases. By properly controlling the electrolytic condition I could always isolate hydroxyimidines as the intermediate reduction product which could not hitherto be prepared by a purely chemical process.

Free phthalimide was electrolytically reducible only in an acid solution, and changed into oxyphthalimidine or phthalimidine according to the electrolytic conditions. In an alkaline solution phthalimide was chiefly hydrolysed into phthalamic acid and phthalic acid and gave no reduction-product. In the case of methyl or ethyl phthalimide intermediate oxyimidines were obtained when electrolysis was conducted in their acid solution with the copper cathode. With the lead cathode reduction went further on so as to produce phthalimidine.

It is here to be noted that so-called oxyphthalimidine prepared purely chemically by A. Reisert⁽¹⁾ differs from that which I prepared by the electrochemical method. While my oxyphthalimidine melts at 105°, that obtained by Reisert is reported to melt at 171°. In studying how they differ from each other it was found that the former can be transformed into the latter, when it was dissolved in 6N-H_2SO_4 at about 75° and then precipitated again by neutralizing sulphuric acid with caustic soda. The substance thus formed crystallized in needles and melted at 170–171°. Its properties were identical with Reisert's oxyphthalimidine in all respects and its melting point showed no depression when mixed with some oxyphthal-

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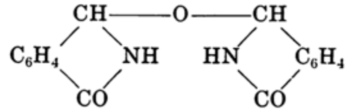
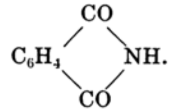
(1) *Ber.*, **46** (1913), 1488.

imidine prepared by reducing phthalimide with zinc and caustic soda. Reisert describes that his oxyphthalimidine changes into an anhydride  by the action of glacial acetic acid. Oxyphthalimidine prepared electrolytically was also found to behave similarly. Now it was made clear from the result of the molecular weight determination that oxyphthalimidine prepared by me is the normal compound, while that obtained by Reisert is a polymerized substance consisting of two molecules.

I. Phthalimide,  By reducing phthalimide chemically with tin and hydrochloric acid C. Graebe(1) could only isolate phthalimidine as the reduction product. But by electrolytic chemical method I could isolate the intermediate reduction product which is to be named hydroxy- or oxyphthalimidine, as is described below.

To an alcoholic hydrochloric acid solution consisting of 50 c.c. of alcohol, 10 c.c. of hydrochloric acid (sp. gr. 1.2) and 50 c.c. of water, 3 grams of phthalimide were added, and the mixture was used as the catholyte. As electrodes lead was used and a current of 2 amp./100 sq. cm. was passed at 20°–30°, maintaining the solution always in agitation. After 4 hours' electrolysis the catholyte coloured greenish yellow was made slightly alkaline by adding a caustic soda solution and cautiously evaporated under a reduced pressure, when a substance which was afterward confirmed to be oxyphthalimidine separated out in a needle form. Exactly the same result was also obtained with an alcoholic sulphuric acid solution in which copper was observed to act as the cathode with similar effect.

The substance separated out as needle crystals was soluble in hot water and alcohol, and difficultly so in benzene and ether. It melted at 105° and was easily transformed into the original substance when oxidized with potassium permanganate and sulphuric acid, and was also reducible further to phthalimidine when a current of a greater density was passed into a more strongly acidic solution. The results of the elementary analysis and of the molecular weight determination were found as follows:

Anal. Subst. $=0.0680$; $CO_2=0.1610$; $H_2O=0.0296$ gr. Found: $C=64.51$; $H=4.84\%$. Calc.: $C=64.43$; $H=4.73\%$.

0.3630 gr. substance produced ammonia which required 6.4 c.c. of 0.3879 N-HCl. Found: $N=9.38\%$. Calc.: $N=9{\cdot}40\%$.

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(1) *Ann.*, **247** (1888), 288.

Its molecular weight was determined by the ebullioscopic method using ethyl alcohol as the solvent.

Subst. = 0.253, solvent = 15.382 gr.; elevation of b.p. = 0.080°. Mol. wt., found: 155, calc.: 149.

Another experiments was next tried making the cathode solution about 5 times more acidic and passing a current of 6 amp./100 sq. cm. for 6–7 hours. The temperature was maintained between 30° and 40°. When the electrolysis was over the electrolytic solution, coloured greenish yellow, was evaporated under a reduced pressure to remove alcohol, and left to stand for a day after having been made slightly alkaline, whereupon phthalimidine separated out as long needle crystals. A sulphuric acid solution consisting of equal volumes of water, alcohol and concentrated sulphuric acid also gave nearly the same results. It is a rather remarkable fact that even the copper cathode produced the same reduction product, but not intermediate oxyphthalimidine, when worked with a strongly acidified cathode solution.

Phthalimidine was purified by recrystallizing it from alcohol and obtained as colourless needles melting at 149°. Its hydrochloride combines with gold trichloride to form a double salt, melting point of which was determined to be 195°. For analysis the gold content of this double chloride was estimated.

0.1590 gr. substance gave on ignition 0.0515 gr. Au. Found: Au = 32.40%. calc.: Au = 32.48%.

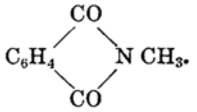
As was stated before, oxyphthalimidine prepared electrochemically changes into the so-called oxyphthalimidine obtained by Reisert by a purely chemical method. Though the latter has higher melting point its chemical properties are nearly the same with those of the former, changing to phthalimide on oxidation and to phthalimidine on reduction. On determining its molecular weight by the ebullioscopic method it was found to be a polymerized substance consisting of two molecules, thus:—

Subst. = 0.256, solvent = 19.05 gr.; elevation of b.p. = 0.052°. Mol. wt., found: 302, calc.: 298.

Reisert states that his oxyphthalimidine changes into an anhydride melting at 240° when boiled with glacial acetic acid. It was now found that normal oxyphthalimidine, just like the polymerized substance, may also be transformed into the same anhydride when treated with 6 normal sulphuric acid heated above 75°. The molecular weight of the anhydride was also determined by the boiling point method as follows:

Subst. = 0.110, solvent = 15.33 gr.; elevation of b.p. = 0.030°. Mol. wt., found: 280, calc.: 281.

A series of experiments were carried out electrolytically to reduce phthalimide in a solution of about 2 normal caustic soda, but in no case reduction products could be isolated. It was observed that phthalimide easily undergoes hydrolysis and changes into phthalamic acid and further to phthalic acid.

II. Methyl Phthalimide,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\,CH_3$. The electrolytic reduction of methyl phthalimide in a sulphuric acid solution was first undertaken using lead as the cathode. As the catholyte a mixture of 50 c.c. of water, 40 c.c. of absolute alcohol and 10 c.c. of 95% sulphuric acid was used, and for 2 gr. of the imide a current of 3 amp./100 sq. cm. was passed for 3 hours at 25°. When the electrolysis was over, the cathode solution was evaporated to drive off alcohol and made alkaline by adding a caustic soda solution, whereupon a reduction-product separated out in an oily form. It was extracted with ether and recrystallized from alcohol. It crystallized in plates having a characteristic odour and melting at 45°. It was analysed as its gold double chloride which melted at 145°.

0.1215 gr. substance gave 0.0492 gr. gold on ignition. Found: Au = 40.5%. calc.: Au = 40.6%.

The reduction product was thus confirmed to be methyl phthalimidine.

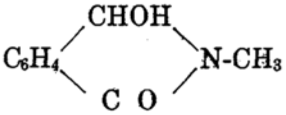
When copper was used as the cathode maintaining other conditions the same no imidine was formed, but a quite new reduction product was obtained. It crystallized in a short prismatic form from hot water and melted at 129°. It was soluble in alcohol, ether, acetone and benzene. It was reducible into corresponding phthalimidine electrolytically with the lead cathode and chemically with zinc and sulphuric acid, and was oxidizable to methyl phthalimide by the action of potassium permanganate and sulphuric acid. The result of the elementary analysis was found to be as follows:

Anal. Subst. = 0.0880; CO_2 = 0.2140; H_2O = 0.0435 gr. 0.4014 gr. substance produced ammonia, neutralization of which required 6.5 c.c. of 0.3879 N-HCl. Found: C = 66.34; H = 5.53; N = 8.67%. calc. for $C_9H_9O_2N$: C = 66.26; H = 5.52; N = 8.59%.

Its molecular weight was determined by the ebullioscopic method using alcohol as the solvent.

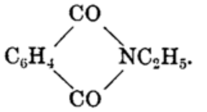
Subst. = 0.2276, alcohol = 16.237 gr.; elevation of b.p. = 0.105°. Mol. wt., found: 157, calc.: 163.

From these results it may be concluded that the reduction product is nothing but oxyphthalimidine having the formula



The electrolytic reduction in a hydrochloric acid solution was observed to proceed in the similar way and perhaps more easily.

No reduction product could be isolated in the electrolysis conducted with an alkaline solution, in which all phthalimide completely hydrolysed into phthalic acid and methylamine.



III. Ethyl Phthalimide, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NC_2H_5$. The electrolytic reduction of ethyl phthalimide in an alcoholic sulphuric acid solution was carried out in the manner just analogous to the case of methyl phthalimide. By using lead as the cathode ethylphthalimidine was obtained as a colourless oil having a characteristic odour. It was analysed as gold double chloride melting at 145°. When copper or nickel was used as the cathode no ethyl phthalimidine was formed, but ethyloxyphthalimidine was produced instead of it. It is soluble in water, alcohol, ether, acetone and benzene, and melts at 106°. It was analysed with the following results:

Anal. Subst.=0.1060; CO_2=0.2635; H_2O=0.0600 gr. 0.3982 gr. substance gave ammonia which required 4.15 c.c. of 0.5447 N-HCl for neutralization. Found: C=67.78; H=6.33; N=7.93%. calc. for $C_{10}H_{11}O_2N$: C=67.80; H=6.27; N=7.91%.

The molecular weight was determined with the ebullioscopic method using benzene as the solvent.

Subst.=0.1375, benzene=21.70 gr.; elevation of b.p.=0.090°. Mol. wt., found: 184, calc.: 177.

It was transformed into ethyl phthalimidine when further reduced with a lead cathode in a sulphuric acid solution, and into ethyl phthalimide when electrolytically oxidized with a platinum anode in an acetone sulphuric acid solution.

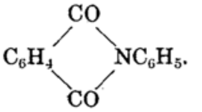
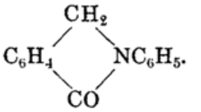
The electrolysis in a caustic soda solution gave no reduction product and produced ethyl phthalamic acid as a product of hydrolysis. It was isolated from the cathode solution by acidifying it with hydrochloric acid. It crystallized in needles and melted at 136°. It was soluble in hot water, sparingly so in cold. For confirmation its elementary analysis and molecular weight determination were conducted, and the following results were obtained:

Anal. Subst. = 0.1368; $CO_2 = 0.3110$; $H_2O = 0.0704$ gr. 1.3291 gr. substance produced ammonia which required 12.90 c.c. of 0.5447 N-HCl for neutralization. Found: C = 62.02; H = 5.76; N = 7.40%. Calc. for $C_{10}H_{11}O_3N$: C = 62.14; H = 5.74; N = 7.25%.

The molecular weight was determined ebullioscopically using alcohol as the solvent.

Subst. = 0.0584, alcohol = 17.48 gr.; elevation of b.p. = 0.018°. Mol. wt., found: 199, calc.: 193.

Phthalic acid and ethylamine were also formed as the products of hydrolysis.

IV. Phenyl-phthalimide,  $C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}NC_6H_5$. The electrolytic condition was maintained nearly the same as in the previous electrolysis, except that the temperature of the bath was kept a little higher, that is, at 85°. After the electrolysis the solution was filtered while hot and left to cool, when shining scaly crystals separated out. The crystal was insoluble in water and ether, but soluble in hot alcohol and benzene, and it was confirmed to be phenyl phthalimidine  $C_6H_4\genfrac{<}{>}{0pt}{}{CH_2}{CO}NC_6H_5$.

Several trials were made to isolate oxyphenylphthalimidine as the intermediate reduction-product by changing the conditions of electrolysis in different ways, but all was fruitless.

The electrolysis in an alkaline solution yielded no reduction product, phenylphthalimide hydrolysing easily and completely into phthalic acid and aniline.

My hearty thanks are due to Professor Motooki Matsui, under whose kind guidance and encouragement the work was carried out.

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Kyoto Imperial University.