ELECTROLYTIC REDUCTION OF ALKYLPHTHALIMIDES.
II. PHTHALIC ANHYDRIDE.

By **Buhei SAKURAI.**

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Phthalic anhydride was reported by J. Wislicenus⁽¹⁾ to give several reduction products, such as diphthalyl, phthalide, hydrodiphthalyl and dihydrophthalyl lactonic acid, when reduced with glacial acetic acid and zinc, while A. Reisert⁽²⁾ obtained only diphthalyl lactonic acid by reducing phthalic anhydride with a mixture of potassium chloride, alcohol and zinc dust. On comparing these reduction products produced by a purely chemical method with those obtained by electrochemical reduction of phthalimide reported in the present writer's previous communication,⁽³⁾ it was deemed very interesting to study how reduction of phthalic anhydride really takes place electro-chemically.

In an experiment conducted with an ammonium carbonate solution using lead as the cathode, reduction of phthalic anhydride to phthalide was observed to take place smoothly at high temperatures. Evidently phthalic anhydride changed into ammonium phthalate before it was reduced, and the catholyte remained always slightly alkaline till the end of the electrolysis. Besides lead, metals having moderate overvoltage for hydrogen, such as nickel and copper could be used with nearly the same efficiency.

Reduction in a sodium bicarbonate solution was accomplished with difficulty. Electrolysis was conducted by passing a constant current of carbon dioxide into the catholyte with the object of preventing it from becoming too alkaline. At comparatively low temperatures such as 30°—40° C., a small quantity of phthalide was produced as the reduction product, which gradually decreased as the temperature rose, till at last at tempera-

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(1) *Ber.*, **17** (1884), 2178.
(2) *Ber.*, **46** (1913), 1484.
(3) This Bulletin, **5** (1930), 184.

tures above 70°C., the reduction completely came to an end. The reason why the reduction does not proceed at high temperatures is not difficult to find, if we suppose that too strong alkalinity of the catholyte is unfavourable to the reduction. Experimentally to confirm whether this supposition be true or not, electrolysis of a sodium or potassium phthalate was once by itself and once by constantly neutralizing a greater part of alkali set free in the catholyte with hydrochloric acid. As was expected, no reduction product was formed in the former case, while in the latter phthalide was obtained with a moderate yield.

Reduction of phthalic anhydride in an acid solution was also undertaken, but all efforts to procure the reduction products turned out fruitless.

Throughout all experiments the reduction product was always found to be phthalide, and neither oxyphthalide nor other reduction products chemically got by Wislicenus could be isolated. So it was attempted to obtain reduction products other than phthalide, by controlling the temperature and the current density and also by using many different metals as the cathode. All these trials were, however, made in vain, producing in no case, any other reduction product.

Electrolysis was also carried out with the bath previously mixed with some phenyl-hydrazine to see if some intermediated product such as oxyphthalide could be isolated in some form combined with the hydrazine. This expectation was also betrayed, nothing but α-phthalyl benzyl hydrazine been obtained.

Experimental.

1. Ammonium Carbonate Solution as the Catholyte. Experiment was conducted under the following conditions:

Anode: lead; Anode solution: a saturated ammonium carbonate solution; Cathode: lead (200 sq. cm.); Catholyte: 40 c.c. of saturated ammonium carbonate solution + 80 c.c. of alcohol + 10 gr. of phthalic anhydride; Current density: 2 amp./100 sq. cm.; Temperature: 75°—80°C.

After an hour's electrolysis the catholyte which always remained slightly alkaline was acidified with hydrochloric acid and evaporated to drive off alcohol, whereupon about 2.3 gr. of the white tabular crystal of phthalide separated out. The yield is calculated to be 25%. It was increased to 85% by 3 hour's electrolysis and to 96% by continuing it still 2 hour's longer.

2. Ammonium Phthalate Solution as the Catholyte. A solution containing 10 gr. of ammonium phthalate in 100 c.c. was taken as the catholyte and 5% ammonia water as the anolyte, and electrolysis was carried out for 2 hours under the conditions as in 1. On cooling the catholyte after acidifying it with hydrochloric acid, about 6 gr. of phthalide were isolated. The yield corresponds to 90% of the theoretical.

3. **Ammonium Acetate Solution as the Catholyte.** Five grams of phthalic anhydride dissolved in a mixture of 40 c.c. of 10% ammonium acetate and 80 c.c. of alcohol was electrolysed in an analogous manner as in 1, taking 10% ammonium acetate solution as the anolyte. The yield of phthalide was found to be 33%.

4. **Sodium Bicarbonate Solution as the Catholyte.** It was first supposed that the use of a sodium bicarbonate solution would be suitable for the reduction of phthalic anhydride, as the alkalinity of the solution might be kept nearly unaltered simply by passing carbon dioxide to the catholyte. But it soon became clear that such was not really the case. For phthalic anhydride is hardly soluble in a saturated sodium bicarbonate solution, and if alcohol is added to the catholyte in order to increase the solubility of the anhydride, it decreases that of the bicarbonate. Elevation of temperature to the neighbourhood of 75°C. increases the solubility of the anhydride, but this makes the catholyte strongly alkaline in spite of a constant influx of carbon dioxide. In short, to keep phthalic anhydride dissolved in a saturated sodium bicarbonate solution without greatly increasing the alkalinity of the solution was hardly practicable, and consequently the electrolytic reduction of phthalic anhydride with this solution produced only a very small quantity of phthalide at 20°–30°C., and no phthalide at 75°C.

5. **Alkali Phthalate Solution as the Catholyte.** Soon after electrolysis was commenced, the catholyte became strongly alkaline, though carbon dioxide was constantly passed into it, and perhaps for this reason no reduction took place. When, however, the same electrolysis was repeated by constantly dropping two normal hydrochloric acid into the catholyte so as to keep it always slightly alkaline, phthalide was obtained with 35% yield.

6. **Acid Solution as the Catholyte.** Electrolytic reduction of phthalic anhydride in an acid solution was attempted by using sulphuric, hydrochloric or acetic acid, concentrated and dilute. But in no case could a substance deemed to be a reduction product be procured.

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Chemical Institute, Osaka Women's College,
Sumiyoshi, Osaka.

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