ELECTROLYTIC REDUCTION OF ALKYLPHTHALIMIDES. III. REDUCTION OF PHTHALIC ANHYDRIDE.

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In the previous experiments[1] it was found that for electrolytic reduction of phthalates electrolysis must be conducted at a higher temperature using a solution not too alkaline. Now with the object of making these relations still clearer an experiment was first carried out to see the influence of temperature on the reduction reaction.

As the catholyte a 5% ammonium phthalate solution was taken, and this was electrolysed, on a constant agitation, with a lead cathode by passing a current of 1.5 amperes for 100 sq. cm. of the cathode. Lead was also chosen as the anode, which dipped to the anolyte consisting of 5% ammonia water. During the course of electrolysis the bath was dipped in water to keep its temperature constant, and when the temperature began to rise 5 degrees higher than the constant temperature, the electric current was cut off for a while to cool the bath again to the constant temperature. The material yields of phthalide after an hour's electrolysis were as follows;

Temperature	50 – 55°	60 – 65°	70 – 75°	80 – 85°
Yield %	very small	6	80	90

Smooth reduction is thus seen to take place only at temperatures higher than 70°C.

Next, to know the effect of the alkalinity of the solution on the reduction, the pH value of the catholyte was constantly observed using Shibata's electrometric titration apparatus prepared by Shimadzu & Co. Three different phthalic anhydride solutions, as shown in the following table, were electrolysed for 90 minutes by passing a current of carbon dioxide at the rate of 60 c.c. per minute, and during the whole course of electrolysis, the pH value in the catholyte was observed at intervals of ten minutes. The results are shown in Tables 1 and 2.

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Table 1.

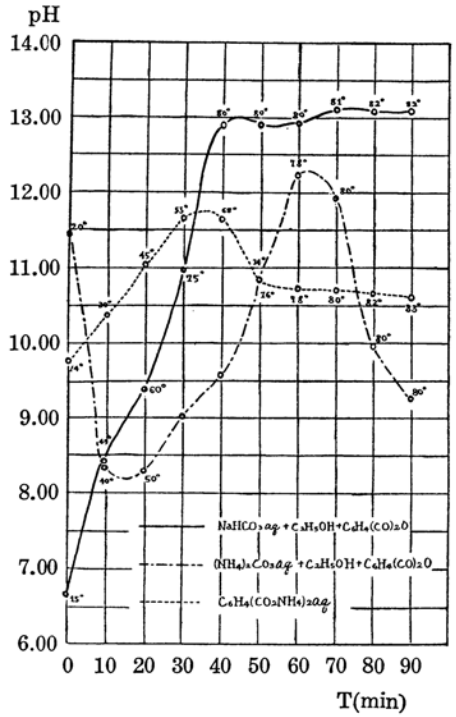
Catholyte	Cathode	Anolyte	Anode	Current density Am./100 sq. cm.	Temp. max.	Time min.	Yield % of phthalide
Satur. $NaHCO_3$ 60 c.c. Alcohol 60 c.c. Phthalic anhyd. 5 gr.	lead	Saturated $NaHCO_3$	lead	1.5	82	90	0
Satur. Am_2CO_3 60 c.c. Alcohol 60 c.c. Phthalic anhyd. 5 gr.	lead	Saturated Am_2CO_3	lead	1.5	80	90	50
Water 120 c.c. Am phthalate 5 gr.	lead	5% ammonia water	lead	1.5	83	90	75

Table 2.

	Sodium bicarbonate		Ammonium carbonate		Ammonium phthalate	
Time of electrolysis (min.)	Temp.	pH	Temp.	pH	Temp.	pH
0	15	6.33	20	11.43	14	9.70
10	45	8.39	40	8.28	30	10.35
20	60	9.28	50	8.26	45	11.00
30	75	10.98	65	9.04	55	11.59
40	80	12.85	73	9.54	68	11.61
50	80	12.80	76	10.85	74	10.83
60	80	12.82	78	12.24	78	10.72
70	81	13.00	80	11.96	80	10.68
80	82	13.00	80	9.96	82	10.62
90	82	13.02	80	9.33	83	10.58

Change of pH value in the course of electrolysis may be traced more clearly in the following figure.

In the electrolysis of the sodium bicarbonate solution, the pH value rapidly increased with temperature, and at temperatures favourable for reduction, the cathode solution became strongly alkline in spite of a constant influx of carbon dioxide gas. The reason phthalic anhydride could not be reduced well in this solution is thus clearly seen.



The ammonium carbonate solution behaves quite differently. In the first stage, the pH value decreases, and from 40°C. upward increases attaining a maximum value of 12 at 78°C. From this point it begins again to decrease, perhaps owing to the evaporation of ammonia, and in this manner the catholyte becomes very suitable for reduction of phthalic anhydride at the temperature, as well as in the condition of the solution.

In the case of ammonium phthalate, change of the hydrogen ion concentration under temperature is comparatively small and gradual, and at the temperatures favourable for reduction, the pH value is always found to be less than 11.

From the above results, that pH value of the electrolytic bath suitable for reduction of phthalic anhydride may roughly be estimated to lie between 10.5—12.

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