Electrolytic Reduction of Naphthalimide and its Derivatives.

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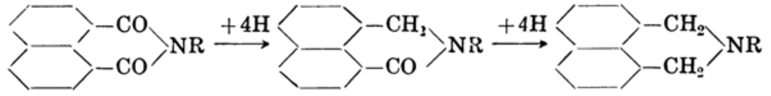
So far as the author is aware, no one has yet succeeded in reducing naphthalic acid imides by purely chemical means. Electrolytically, however, both carbonyls in the imides may successfully be reduced as in the case of other dibasic acid imides, when zinc amalgam⁽¹⁾ is used as the cathode.



I II III R = H, CH_3 or C_2H_5

N-Alkyl-naphthalimide *N*-Alkyl-naphthalimidine *N*-Alkyl-hydrobenzoisoquinoline

In the reduction experiments E. Späth⁽²⁾ and his collaborator used lead cathode in a 50% sulphuric acid solution passing the current of 45 amp. per 100 sq. cm., and reported to have obtained 15% hydrobenzoisoquinoline as the final reduction product. By working under exactly the same condition the author could procure no reduction product, and even with the cathode of zinc amalgam the result was not much improved.

In order to find out better conditions for electrolytic reduction several experiments were performed by controlling concentration of sulphuric acid, current density, temperature of electrolyte, etc., but all were fruitless. Influence of alcohol added to the electrolyte with the object of increasing the solubility of the imide was found out to bring no better results.

In the case of its derivatives such as *N*-methyl-naphthalimide and *N*-ethyl-naphthalimide reduction took place with much ease. They were reduced with fairly good yield in sulphuric acid solution with cathode and produced *N*-methyl-naphthalimidine and *N*-ethyl-naphthalimidine respectively. The reduction stopped here without going further than this stage. For their complete reduction cathode of much stronger reducing power, such as zinc amalgam was required.

Experimental.

The materials used in the experiment were prepared in the following way.

Naphthalic acid was first prepared from acenaphthene by oxidizing it with powdered potassium bichromate in a warm glacial acetic acid solution, and naphthalic acid anhydride thus obtained (yellow powder, melting at 270°) was heated in a retort to which a current of ammonia was constantly passed and then cooled till it became

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(1) B. Sakurai, this Bulletin, **7** (1932), 155; **10** (1935), 311.

(2) E. Spàth and F. Brausch, *Univ. Wien, Monatschr.*, **50** (1928), 349.

a lump. The lump was taken out and crushed into powder and recrystallized from alcohol. Naphthalimide was thus prepared as reddish-brown powder, melting at 300°.

Methyl-naphthalimide was prepared by mixing naphthalic acid anhydride and methylamine in equivalent amount and recrystallized from alcohol after it was gradually heated on the water bath (yellow brown needle-like crystals, melting at 205°). Ethyl-naphthalimide (yellow needle-like crystals, m.p. 148°) was prepared in the same manner using ethylamine instead of methylamine.

I. **Naphthalimide** (I, R=H). Naphthalimide and its derivatives are insoluble in sulphuric acid solution. When one or both of two carbonyl groups are reduced into methylene groups, the basicity of molecules increases considerably, and in consequence they become soluble in the acidic electrolyte forming soluble salt. Thus the progress of reduction is clearly indicated by gradual disappearance of the imides suspended in the electrolyte. The experiments were conducted with lead cathode by controlling concentration of sulphuric acid (30–90%), temperature (26–60°), and current density (5–12 amp. per 100 sq. cm.), in various manners, but in no case the material was seen to dissolve in electrolyte. As the reduction was perceived to take place with zinc amalgam cathode, the best conditions of electrolysis were sought as follows. Cathode: zinc amalgam, 16 sq. cm. of area. Catholyte: mixture of 50 c.c. of 90% H_2SO_4 and 50 c.c. of alcohol and 1 g. of naphthalimide was added to it. Anode: cylindrical lead plate. Anolyte: 90% H_2SO_4. Current density: 105.3 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 1234.9 F. per mol. Temperature: 30°.

Into the anolyte contained in a cylindrical biscuit vessel a cell containing catholyte was dipped, and a spiral lead tube was inserted into the cathode chamber. Cold water was passed through the tube to cool catholyte from inside, while the electrolyte bath itself was cooled all the time from outside with cold water. After 10 hours' electrolysis the catholyte still containing a considerable amount of undissolved substance was taken out and heated on the water bath to drive off alcohol. It was then diluted with about three times as much water and filtered. 0.69 g. of unreduced substance was obtained. The acidic solution was then shaken with ether several times in order to extract original imide remaining unreduced. About 0.14 g. of another unreduced substance was obtained. The aqueous solution was then made alkaline with caustic soda and treated with ether yielding thereby a small quantity of a brownish substance.

The platinum double chloride of this substance melted at 198° with decomposition. (Found: Pt, 26.04. Calculated for $[C_{12}H_{11}N]_2H_2PtCl_6$: Pt, 26.10%). The yield of the dihydrobenzoisoquinoline was found to be 8%.

II. **N-methyl-naphthalimide** (I, $R=CH_3$). (1) *Reduction with lead cathode.* With the view of obtaining *N*-methyl-naphthalimidine, reduction was conducted in sulphuric acid solution with lead cathode under the following conditions. Cathode: cylindrical lead plate, 100 sq. cm. of area. Catholyte: 1 g. of imide was suspended in 100 c.c. of 50% H_2SO_4. Anode: cylindrical lead plate. Anolyte: 50% H_2SO_4. Current density: 5 amp. per 100 sq. cm. Current quantity: 393.6 F. per mol. Temperature: 40°.

The electrolysis was carried out by cooling the electrolytic bath from outside with cold water, keeping the catholyte always in a vigorous agitation. The imide appeared to have dissolved fairly well. But 10 hours' electrolysis seemed to have been still insufficient as 0.57 g. of the original imide was detected remaining unchanged. This was filtered, and the filtrate was extracted with ether, when 0.059 g. of some other unreduced substance was obtained. The solution was made alkaline with caustic soda solution and again extracted with ether. About 0.3 g. of brown oily substance with a peculiar smell was obtained. This was easily soluble in hydrochloric acid solution and formed white needle-like crystals. Its platinum double chloride formed orange-coloured crystals melting at 172° with decomposition. (Found: Pt, 24.27. Calculated for $[C_{13}H_{11}NO]_2H_2PtCl_6$: Pt, 24.28%). The substance is thus regarded undoubtedly as *N*-methyl-naphthalimidine.

In the electrolysis with lead cathode reduction seems not to proceed further than the first stage. As the concentration of sulphuric acid has a close relation to reduction rate, a series of experiments were carried out by varying the concentration of sulphuric acid, results of which are summarised in Table 1.

From the table it is seen that the amount of unreduced substance decreases, as the concentration of sulphuric acid increases, making the reduction rate more than 30% in 50% solution of sulphuric acid. If, however, the concentration of sulphuric acid exceeds 50%, the yield of the reduced substance shows no remarkable increase despite the considerable decrease of the undissolved substance. Perhaps this is due to the fact that the imide partly polymerises into an unreducible substance on account of the high concentration of sulphuric acid. A resinous substance which may be regarded as such a polymer was always obtained, when electrolysis was conducted with the catholyte containing more than 70% of sulphuric acid.

Table 1.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-methyl-naphthal-imidine (%)
20	91	—	4.5
30	75	—	14
40	67	—	23
50	57	5	32
60	55	9	30
70	30	21	36
80	20	35	33

As *N*-methyl-naphthalimide is slightly soluble in alcohol, though it is insoluble in sulphuric acid, electrolysis was carried out with a solution to which an equal volume of alcohol was added. The results are shown in Table 2.

As is seen from the table, the solution containing 40% of sulphuric acid gives the best results. When sulphuric acid becomes more concentrated the reduction rate falls rapidly, which shows that the effect of alcohol is rather harmful. Probably alcohol acts to enhance the resinification of the material, which is responsible for the rapid increase of ether extract from acidic medium containing more than 70% sulphuric acid.

Table 2.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-methyl-naphthal-imidine (%)
40	25	10	49
50	30	11	27
60	42	15	19
70	10	60	20
80	13	51	18
90	11	59	22

(2) *Reduction with zinc amalgam cathode.* For the purpose of obtaining the complete reduction product of *N*-methyl-naphthalimide, i.e. *N*-methyl-hydrobenzoisoquinoline, zinc amalgam was taken as the cathode under the following conditions. Cathode: zinc amalgam 16 sq. cm. Catholyte: 100 c.c. of 50% H_2SO_4 in which 1 g. of imide was suspended. Anode: cylindrical lead plate. Anolyte: 50% sulphuric acid. Current density: 75 amp. per 100 sq. cm. Time of electrolysis: 6 hours. Current quantity: 566.9 F. per mol. Temperature: 34°.

Electrolysis was carried out by cooling the electrolytic bath, from outside with cold water and from inside by passing cold water through a spiral lead tube inserted to the catholyte, which was always kept vigorously stirring. Though the imide did not readily dissolve in the electrolyte, yet its amount was observed to diminish by degrees. At the beginning of electrolysis the experiment was much disturbed by hydrogen bubbles evolved at cathode, but it was soon found that this was easily prevented by dropping a small quantity of alcohol into it. After 6 hours' electrolysis the catholyte was diluted with about double volume of water and then filtered, when about 0.55 g. of insoluble substance was isolated. The filtrate was then treated with ether, and from the ether extract a small amount of light yellow fine needle-like crystals was obtained. This substance melted at 205° and was found to be unreduced material.

Now the remaining solution was made alkaline with caustic sode solution and then subjected to steam distillation. After making the distillate acidic with dilute hydrochloric acid it was evaporated to dryness. 0.2 g. of a substance in the form of white powder was left as the residue. That this substance was nothing but the hydrochloride of desired *N*-methyl-hydrobenzoisoquinoline was proved by analysing its platinum double salt obtained as beautiful orange-coloured crystals melting at 212° under decomposition. (Found: Pt, 25.15. Calculated for $[C_{13}H_{13}N]_2H_2PtCl_6$: Pt, 25.15%).

The solution, from which *N*-methyl-hydrobenzoisoquinoline was extracted with ether, was distilled with steam to drive off the base still remaining, and again treated with ether. After evaporating ether from the ether extract the aqueous solution was acidified with hydrochloric acid and evaporated to dryness. 0.05 g. of white powder was yielded. The platinum double chloride of this substance, melting at 170°, was identified as the double salt of *N*-methyl-naphthalimidine formed by electrolysis at lead cathode.

With the view of investigating the relation between the concentration of sulphuric acid and the reduction rate, a series of experiments was carried out by using as catholyte a mixture of equal volume of alcohol and sulphuric acid solution of various concentrations. Each electrolysis was continued for ten hours and the results are as shown in Table 3.

Table 3.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-methyl-hydro-benzo-iso-quinoline (%)	*N*-methyl-naphthal-imidine (%)
50	31	20	21	5.0
60	17	20	26	4.5
70	13	21	29	5.9
80	20	23	27	4.4
90	14	29	38	4.5

As is seen from the above table, the greater was the concentration of acid the less was the undissolved material, and at the same time the more the yield of *N*-methyl-hydrobenzoisoquinoline. The concentration of sulphuric acid seems to exert no influence upon the yield of *N*-methyl-naphthalimidine, which remains almost constant. When the concentration of sulphuric acid becomes more than 70%, the quantity of the ether extract from acidic medium is observed to increase gradually. This is probably due to polymerization of the material, as was stated above.

III. **N-ethyl-naphthalimide** (I, $R=C_2H_5$). (1) *Reduction with lead cathode.* In order to get the reduction product of the first stage, i.e. *N*-ethyl-naphthalimidine, electrolysis was tried with lead cathode under the following conditions. Cathode: cylindrical lead plate, 100 sq. cm. of area. Catholyte: 100 c.c. of 60% sulphuric acid solution in which 1 g. of imide was added. Anode: cylindrical lead. Anolyte: 50% sulphuric acid. Current density: 6.5 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 546 F. per mol. Temperature: 35°.

Electrolysis was conducted just in the same manner as in the case of the methyl derivative. When electrolysis stopped, a great quantity of insoluble substance still remained suspended in the solution. This was filtered off and 0.68 g. of unreduced substance was obtained. The filtrate was then treated with ether and from the ether extract 0.10 g. of unreduced substance was further produced. The electrolyte was then made alkaline with caustic soda and treated with ether, when a small amount of a yellowish oily substance soluble in hydrochloric acid was obtained. Its platinum double chloride was formed as yellow-brown crystals, melting at 165° with decomposition. (Found: Pt, 23.44. Calculated for $[C_{14}H_{13}NO]_2H_2PtCl_6$: Pt, 23.46%).

This reduction product was identified to be *N*-ethyl-naphthalimidine. The reduction rate was calculated to be 15.4%.

The results of investigation carried out to determine the relation between the concentration of sulphuric acid and the reduction rate are summarized in Table 4.

As 80–90% sulphuric acid solution caused foaming of catholyte, which made electrolysis very troublesome, a little amount of alcohol was added to catholyte. In consequence, insoluble substance remarkably decreased, while the part extracted with ether from acid solution increased. The concentration of 60% was found to be most favourable for reduction.

Table 4.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-ethyl-naphthal-imidine (%)
40	82	8	4.5
50	78	10	6.3
60	68	10	15.4
70	75	8	9.1
80	47	30	9.1
90	45	35	10.9

The results of the electrolysis showing the relation of the concentration of sulphuric acid to the reduction rate, when worked with catholyte containing an equal volume of alcohol, are shown in Table 5.

Table 5.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-ethyl-naphthal-imidine (%)
40	92	3	1
50	70	19	2
60	72	15	3
70	68	15	2
80	70	16	2
90	71	18	2

(2) *Reduction with zinc amalgam cathode.* With the view of obtaining the complete reduction product electrolysis was carried out with zinc amalgam cathode under the same conditions as were used in reduction of the corresponding methyl derivative. They were as follows. Cathode: zinc amalgam, 16 sq. cm. of area. Catholyte: mixture of 50 c.c. of 50% H_2SO_4 and 50 c.c. of alcohol in which 1 g. of the imide was introduced. Anode: cylindrical lead plate. Anolyte: 50% H_2SO_4. Current density: 75 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 103.7 F. per mol. Temperature: 26°.

The material dissolved readily in the course of electrolysis and reduction seemed to take place far more smoothly than with lead cathode. But its dissolution was not completed even at the end of electrolysis. The catholyte was heated on the water bath to drive off alcohol and then it was diluted with double volume of water. 0.3 g. of undissolved material thus precipitated was filtered, and the filtrate was treated with ether, when 0.3 g. of unreduced substance was extracted. The filtrate was now made alkaline with caustic soda solution, and subjected to steam distillation, collecting the distillate in dilute hydrochloric acid solution as long as it continued to react alkaline. The hydrochloric acid solution was then evaporated to dryness on the water bath, when 0.21 g. of white powder was left as the residue. The platinum double chloride prepared from the residue was beautiful orange-coloured crystals melting at 197° with decomposition. (Found: Pt, 24.29. Calculated for $[C_{11}H_{15}N]_2H_2PtCl_6$: Pt, 24.28%).

On treating the remaining solution after steam distillation with ether a small amount of oily substance was extracted. Its platinum double chloride melted at 165° and was identified as N-ethyl-naphthalimidine. The yield was 5.4%. In order to obtain the relation of the reduction rate to the concentration of acid, a series of electrolyses were carried out by varying the concentration of acid. The results are summarized in Table 6.

Table 6.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-ethyl-hydrobenzo-isoquinoline (%)	*N*-ethyl-naphthalimidine (%)
30	47	19	24	5.1
40	37	25	18	2.2
50	30	30	21	5.4
60	25	31	14	5.4
70	23	31	15	5.4
80	21	33	17	5.4
90	—	30	44	6.1

As is seen from the table, the greater was the concentration of the acid, the more soluble became the material, and at 90% it completely dissolved, but the ether extract did not increase in the same proportion. The yield of the complete reduction product remarkably increased at 90%. The yield of *N*-ethyl-naphthalimidine, independent of the concentration of acid, remained nearly constant, as in the case of the corresponding methyl derivative.

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