

# Electrolytic Reactions of Naphthalene and its Derivatives. Part I.

## Electrolytic Oxidation of Naphthalene

By

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A. Panchaud de Bottens<sup>(1)</sup> obtained, by the electrolytic oxidation of naphthalene, a small quantity of  $\alpha$ -naphthoquinone and a brown oxidation product of an unknown composition when he used sulphuric acid-acetone solution with platinum and lead electrodes, while he obtained a very small quantity of phthalic acid by using sulphuric acid-acetic acid solution with platinum electrodes. There is apparently no record in chemical literature of the details of the progress of this electrolytic oxidation and the influence of the external conditions upon the reaction.

I have undertaken, in the detailed investigation reported in the present paper, to clear up the true nature of the electrolytic oxidation of naphthalene and its derivatives by studying, above all, the influence of the concentration of sulphuric acid, the current density, the temperature, the nature of the oxygen-carrier and of the solvent, etc., upon the process of the oxidation reaction.

According to my experiments, the electrolytic oxidation of naphthalene takes place only in an acid (sulphuric acid-acetone or sulphuric acid-acetic acid) solution; in an alkaline solution (50 c.c. of 20% sodium hydroxide, 100 c.c. of acetone and 3.8 grams naphthalene with platinum electrodes) no appreciable reaction is observed. The yield

of  $\alpha$ -naphthoquinone and the oxidation efficiency is greater in a sulphuric acid-acetone solution than in a sulphuric acid-acetic acid solution. As the anode material, platinum, lead-peroxide, nickel, lead and iron were used, of which lead-peroxide or platinum gave the best results (Table I). This is due to the higher overvoltage of oxygen evolution, and, especially in the case of lead-peroxide, to its catalytic action as maintained by Müller and Soller.<sup>(2)</sup> The most suitable concentration of sulphuric acid is obtained when it is mixed in the proportion of 20–30 c.c. of sulphuric acid (sp. gr. 1.84) to 100 c.c. of water (Table 2, 3 and 11). I found that the greater the current density is, the higher the oxidation efficiency becomes, but that the production of  $\alpha$ -naphthoquinone with lead-peroxide electrode is greatest at about 2 amp./100 cm.<sup>2</sup> (Table 4), while with platinum electrode it is greatest at about 3 amp./100 cm.<sup>2</sup> (Table 5 and 12). The elevation of the electrolytic temperature always increases the oxidation efficiency, but the production of  $\alpha$ -naphthoquinone does not necessarily go parallel with the elevation of the temperature, and with the lead-peroxide electrode it is found to be better at the room temperature (Table 6). But with the platinum electrode the elevation of temperature and the production of  $\alpha$ -naphthoquinone run parallel (Table 7). At the beginning of this investigation it was expected that a great quantity of  $\alpha$ -naphthoquinone would be prepared by this electrolytic oxidation reaction; but it was soon found that  $\alpha$ -naphthoquinone once produced is not only further oxidized into phthalic acid, but is also polymerised into a dark brown substance. As it is evident from Table 8, the increase of the current quantity is accompanied by the decrease of  $\alpha$ -naphthoquinone and this is evidently due to the faster increase of the side reaction than that of the formation of  $\alpha$ -naphthoquinone.

When a substance, which is easily oxidized by the electric current in the electrolytic oxidation reaction, and is changed into a strong oxidizing agent, is added into the solution of the electrolyte, the oxidation efficiency is made remarkably higher by the catalytic action. As the catalysers of this stamp, the salts of cerium, vanadium, chromium, manganese, ferrocyanides and chlorates are generally used.<sup>(3)</sup>

There are patents for using cerium,<sup>(4)</sup> vanadium<sup>(5)</sup> and chromium<sup>(6)</sup> compounds as oxygen-carriers in the electrolytic oxidation of naphthalene.

I have found the following substances to be effective in the order given:—Cerium nitrate, vanadic acid, potassium chlorate, potassium

chromate, manganese sulphate, potassium ferrocyanide, chrome-alum, etc. (Table 9, 10 and 13).

It is already known that naphthalene gives first  $\alpha$ -naphthoquinone and then phthalonic acid and at last phthalic acid by the pure chemical oxidation<sup>(7)</sup> reaction. In my preliminary experiment I obtained among the products,  $\alpha$ -naphthoquinone and phthalic acid. This fact induces me to assume that the same steps are followed in the electrolytic oxidation of naphthalene as in the purely chemical oxidation. The only question is whether  $\alpha$ -naphthoquinone is directly produced by the oxidation of naphthalene without any intermediate product. In the degree of oxidation, quinones may be considered to be in a similar stage as ketones and aldehydes. A quinone may be, therefore, expected to be obtained by the oxidation of a phenolic compound, as ketones and aldehydes are produced by the oxidation of alcohols. R. Leeds<sup>(8)</sup> has already observed that the aromatic compounds are transformed into the hydroxy-derivatives by the purely chemical oxidation. He has thus obtained phenol from benzene and naphthol from naphthalene. It has been also shown that by the electrolytic oxidation of benzene, phenol<sup>(9)</sup> and benzoic acid,<sup>(10)</sup> there are produced catechol and 2-5-dihydroxy-benzoic acid, etc.

By the colour reaction toward ferric chloride and bleaching powder I have qualitatively confirmed the presence of  $\alpha$ -naphthol in the electrolytic solution as the intermediate product of the oxidation. By the steam distillation of the products of the electrolytic oxidation of naphthalene, a red substance is obtained which is presumably identical with the compound of  $\alpha$ -naphthol and  $\alpha$ -naphthoquinone obtainable by the electrolytic oxidation of  $\alpha$ -naphthol. Thus it appears natural to conclude that naphthalene is oxidized at the first stage into  $\alpha$ -naphthol.

In all my experiments I have found that a considerable quantity of a dark brown resinous substance was produced. A. Panchaud de Bottens<sup>(1)</sup> recognized the same substance and tried in vain to reduce it with phosphorus and hydroiodic acid in order to confirm its properties. This resinous substance easily dissolves in alkali, and is precipitated again by acids. It gives a brownish blue colouration with ferric chloride and its alkaline solution lathers like soap. From these facts it may be inferred that the resinous substance contains the phenolic hydroxy group in its molecule.

I have obtained a small quantity of phthalic acid and a little

larger quantity of an insoluble black substance by the potash fusion of the resinous substance. A still larger quantity of phthalic acid was obtained by the oxidation with alkaline potassium permanganate. From these facts it can be expected that the resinous substance contains a naphthalene ring or a naphthoquinone ring. By distilling with zinc dust I have obtained a compound with yellowish blue fluorescence in the benzene solution. By converting it into the picric acid compound, it was found to consist of  $\alpha\alpha$ -binaphthyl and  $\beta\beta$ -binaphthyl. It can be thus presumed that condensation products of naphthalene exist in the resinous substance. From the facts that  $\alpha$ -naphthol exists in the electrolytic solution and the brownish black substance possesses the phenolic property, there is little room to doubt that  $\alpha\alpha$ -binaphthol is produced as a step in the oxidation, as it is well known that  $\alpha\alpha$ -binaphthol is produced by the oxidation of  $\alpha$ -naphthol with ferric chloride<sup>(11)</sup> and gives  $\alpha\alpha$ -binaphthyl by the zinc dust distillation.

Besides, C. Liebermann<sup>(12)</sup> observed that  $\alpha$ -naphthoquinone is easily condensed into  $\beta\beta$ -binaphthyl- $\alpha$ -diquinhydrone, the latter being transformed into  $\beta\beta$ -binaphthyl by the zinc dust distillation and into phthalic acid by oxidation. Judging from the above behaviours, there is hardly room to doubt the formation of  $\beta\beta$ -binaphthyl- $\alpha$ -diquinhydrone as the intermediate product in this electrolytic oxidation. The smaller yield of  $\alpha$ -naphthoquinone when acetic acid is used as the solvent, is perhaps due to the fact that  $\alpha$ -naphthoquinone, produced by the electrolytic oxidation, is in a more suitable condition to change further to  $\beta\beta$ -binaphthyl- $\alpha$ -diquinhydrone.

On oxidizing the dark brown substance by the method of J. Stenhouse and C. Groves<sup>(13)</sup> I have obtained a small quantity of  $\alpha$ -naphthoquinone,  $\beta\beta$ -binaphthyl- $\alpha$ -diquinone and a larger quantity of violet brown oxidation product.

I have now under investigation this dark brown resinous substance, and judging from the above results, I believe that the existence of  $\alpha\alpha$ -binaphthol and  $\beta\beta$ -binaphthyl- $\alpha$ -diquinhydrone in it is unquestionable.

From these results I venture to assume that the progress of reaction of the electrolytic oxidation of naphthalene may be represented by the following scheme :



### Experimental Part

The refined naphthalene sold by druggists was further refined several times by the sublimation method. This substance melting at  $80^{\circ}$ , and its picrate melting at  $149^{\circ}$ , was used in the following experiments.

#### I. Preliminary Experiment

In order to ascertain what sort of substance is produced by the electrolytic oxidation of naphthalene, the following experiment were performed.

1. The anode liquid consisting of 50 c.c. sulphuric acid (20%), 150 c.c. of acetone and 5 grams of naphthalene was introduced into a beaker. A porous cell, successively washed with 1% alkali, water, 5% hydrochloric acid, and water, was placed in it as the cathode compartment. Sulphuric acid (20%) was taken as the cathode liquid, and a sheet of lead peroxide about  $6.5 \times 8.0$  cm. served as the anode, while a sheet of lead served as the cathode. The beaker was cooled with water to keep the temperature of the bath always at about  $20^{\circ}$ . The electrolysis was continued for nearly 6 ampère hours with a current of 1.0 ampère.

After electrolysis the anode liquid was first extracted with ether and then with benzene. Each solvent was then evaporated, and the residues were mixed together and subjected to steam distillation. The distillation product that came out first was a white crystalline mass, then came out a yellow crystalline substance and at last red crystals in a very small quantity. The crystals were identified as  $\alpha$ -naphthoquinone by the colour reactions with alcoholic phenylhydrazine<sup>(14)</sup> and with alcoholic aniline.<sup>(15)</sup> This was separated from the unchanged naphthalene by using light petroleum ether as solvent and was recrystallized several times from petroleum ether. It now melted at  $125^{\circ}$ . It was further characterized as oxime by heating with hydroxylamine hydrochloride by the method of H. Goldschmidt and H. Smidt.<sup>(16)</sup>

After cooling and separating the dark brown substance from the residue of the steam distillation, the liquid was extracted with a larger quantity of ether and was decolourized with animal charcoal. The ether was then evaporated off and the residue was sublimed, when a

small quantity of white crystalline needles was obtained. The melting point was found to be  $128^{\circ}$  and the substance was proved by the fluorescence reaction to be phthalic acid anhydride.

2. A sulphuric acid-acetic acid solution was tried under the following condition using the same apparatus as before :

Anode solution : 3 gr. naphthalene  
150 c.c. glacial acetic acid  
50 c.c.  $\text{H}_2\text{SO}_4$  (20%)  
Anode : Platinum (5.0  $\times$  8.0 cm.)  
Cathode solution :  $\text{H}_2\text{SO}_4$  (20%)  
Cathode : Spiral platinum  
Current strength : 0.5 ampère  
Current quantity : 7.0 ampère hours.

After separating the crystals from the distillate which was obtained in the same manner as in (I), a product was obtained by neutralizing the filtrate with crystallized sodium carbonate. The crystals and this new product were then mixed together.  $\alpha$ -Naphthoquinone was detected in this mixture. Phthalic acid was detected in the residue of the steam distillation.

## II. *Quantitative Investigation of the Oxidation Products*

Having now confirmed the fact that naphthalene can be oxidized into  $\alpha$ -naphthoquinone and phthalic acid in the acid solution, I next attempted to determine the quantitative relations under various conditions. For this purpose the electrolysis was carried out in a closed apparatus (Fig. I) and a porous cell served as the anode compartment and the outer side of the cathode compartment was cooled or warmed to keep it at a definite temperature.

### A. *Electrolytic Oxidation in Sulphuric acid-acetone Solution*

#### I. Influence of the anode material.

Anode solution : 3.8 gr. naphthalene  
100 c.c. acetone  
50 c.c.  $\text{H}_2\text{SO}_4$  (20 c.c. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 100 c.c. of water)  
Cathode solution :  $\text{H}_2\text{SO}_4$  (The same concentration as in the anode solution)

Temperature: 18–23°.

The  $\alpha$ -naphthoquinone obtained was estimated by K. H. Meyer's method<sup>(17)</sup> and the phthalic acid was identified with the fluorescence reaction. In the Table the oxidizing efficiency is represented by the ratio of the oxidized naphthalene to the naphthalene taken.

Fig. 1.

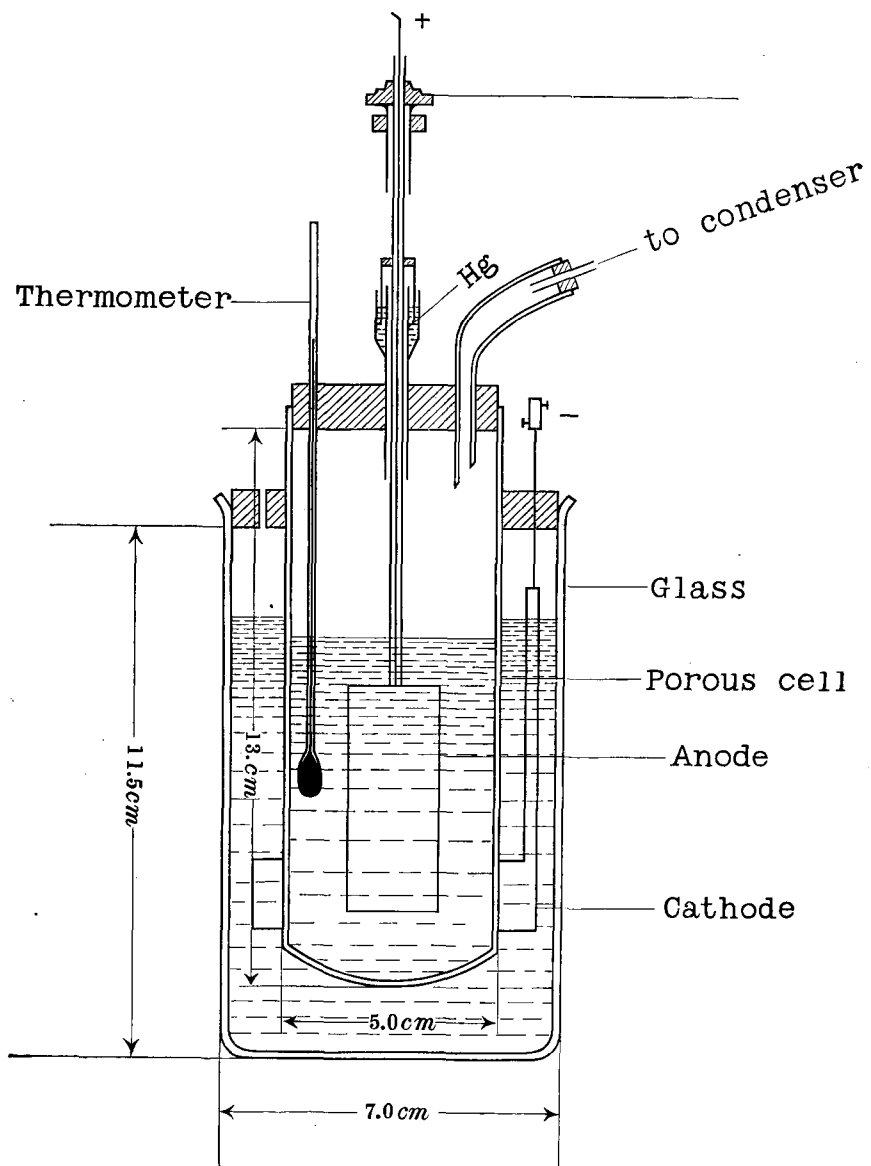




Table I.

Anode material	Anode surface area	Cathode material	Current strength		Current quantity	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Phthalic acid	Oxidizing efficiency
			Amp.	Volt							
	sq. cm.	Spiral	amp.	Volt	amp. hrs.	gr.	%	gr.	gr.		%
Platinum .....	51.40	platinum	1.0	3.0—3.3	4.7	1.5716	3.25	0.1501	1.8397	+	58.64
Lead peroxide	55.40	Lead	1.1	3.1—3.3	4.73	1.5079	6.97	0.3240	1.9352	+	60.34
Nickel .....	40.99	Nickel	0.8	3.2—3.4	4.8	2.3727	0.95	0.0470	1.0712	-	37.56
Lead .....	55.40	Platinum	1.1	3.1—3.2	4.73	1.7575	2.42	0.1185	1.8256	+	53.75
Iron .....	45.55	Platinum	0.9	2.5—2.8	4.68	1.9612	2.08	0.0956	1.5833	-	48.39

II. Influence of the concentration of sulphuric acid.

Anode solution : 3.8 gr. naphthalene

100 c.c. acetone

50 c.c.  $H_2SO_4$

Anode : Lead peroxide

Cathode solution :  $H_2SO_4$  (the same concentration as in the anode solution)

Cathode : Lead

Temperature : 18—23°

Current strength : 0.8 ampère

Current quantity : 4.73 ampère hours.

Table II.

Concentration of sulphuric acid		Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Oxidizing efficiency
Sulphuric acid	Water						
cm.	cm.	volt	gr.	%	gr.	gr.	%
10	100	2.8—2.9	1.7662	3.44	0.1660	1.6781	53.52
20	100	2.9—3.1	1.6473	5.44	0.2529	1.7205	56.65
30	100	3.0—3.2	1.7392	3.79	0.1660	1.6924	54.23
40	100	3.0—3.2	1.9805	2.04	0.0948	1.5147	47.88
50	100	3.2—3.4	1.0850	1.70	0.0790	1.4390	45.12

Anode solution : 2.0 gr. naphthalene

100 c.c. acetone

50 c.c.  $H_2SO_4$

Anode : Platinum

Cathode solution :  $\text{H}_2\text{SO}_4$  (The same concentration as in the anode solution)

Cathode : Spiral platinum

Temperature :  $18-23^\circ$

Current strength : 1.0 ampère

Current quantity : 2.4 ampère hours.

Table III.

Concentration of sulphuric acid		Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Oxidizing efficiency
Sulphuric acid	Water						
cm.	cm.	volt	gr.	%	gr.	gr.	%
10	100	3.0—3.1	1.0192	1.82	0.0434	0.8253	49.04
20	100	3.0—3.3	0.8210	3.36	0.0790	0.9675	58.95
30	100	3.2—3.5	1.0170	2.85	0.0671	0.8002	49.15
40	100	3.4—3.7	1.2408	2.18	0.0513	0.5149	37.96
50	100	3.6—3.8	1.3476	1.68	0.0395	0.4381	32.62

### III Influence of current density.

Anode solution : 3.8 gr. naphthalene

100 c.c. acetone

50 c.c.  $\text{H}_2\text{SO}_4$  (20 c.c. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 100 c.c. of water)

Anode : Lead peroxide

Cathode solution :  $\text{H}_2\text{SO}_4$  (The same concentration as in the anode solution)

Cathode : Lead

Temperature :  $18-23^\circ$ .

Table IV.

Current strength	Voltage	Current quantity	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Oxidizing efficiency
amp.	volt	amp. hr.	gr.	%	gr.	gr.	%
0.6	2.7—2.9	4.698	1.8772	3.42	0.1580	1.6479	50.60
1.1	3.1—3.3	4.730	1.5079	6.97	0.3240	1.9352	66.34
1.6	3.8—4.1	4.800	1.4379	5.03	0.2371	1.9500	62.16
2.2	4.2—4.5	4.600	1.3877	2.62	0.1185	2.1047	63.48

Anode solution : 2.0 gr. naphthalene  
 100 c.c. acetone  
 50 c.c. H<sub>2</sub>SO<sub>4</sub> (The same concentration as  
 in the previous experiment)

Anode : Platinum

Cathode solution : H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the  
 anode solution)

Cathode : Spiral platinum

Current quantity : 2.4 ampère hours

Temperature : 18–23°.

Table V.

Current strength	Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphtho-quinone	$\alpha$ -naphtho-quinone	Dark brown substance	Oxidizing efficiency
amp.	volt	gr.	%	gr.	gr.	%
0.5	2.8–3.1	1.0270	1.98	0.0466	0.8728	48.65
1.0	3.0–3.3	0.8210	3.36	0.0790	0.9675	58.95
1.5	3.4–3.6	0.7136	4.18	0.0984	1.0137	64.32
2.0	3.5–3.8	0.6684	3.55	0.0834	1.0503	66.58
2.5	4.0–4.2	0.6392	3.10	0.0730	1.1026	68.04

IV Influence of electrolytic temperature.

Anode solution : 3.8 gr. naphthalene  
 100 c.c. acetone  
 50 c.c. H<sub>2</sub>SO<sub>4</sub> (The same concentration as  
 in the previous experiment)

Anode : Lead peroxide

Cathode solution : H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the  
 anode solution)

Cathode : Lead

Current strength : 1.1 ampère

Current quantity : 4.73 ampère hours.

Table VI.

Temperature	Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphtho-quinone	$\alpha$ -naphtho-quinone	Dark brown substance	Oxidizing efficiency
°c.	volt	gr.	%	gr.	gr.	%
18–23	3.1–3.3	1.5079	6.97	0.3240	1.9352	60.34
41–47	3.2–3.8	1.2821	5.62	0.2608	2.0406	66.26
55–67	3.6–4.2	1.2061	4.57	0.2122	2.1366	68.26

Anode solution : 2.0 gr. naphthalene  
 100 c.c. acetone  
 50 c.c. H<sub>2</sub>SO<sub>4</sub> (The same concentration as  
 in the previous experiment)

Anode : Platinum

Cathode solution : H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the  
 anode solution)

Cathode : Spiral platinum

Current strength : 1.0 ampère

Current quantity : 2.4 ampère hours.

Table VII.

Temperature	Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Oxidizing efficiency
°c.	volt.	gr.	%	gr.	gr.	%
18—23	3.0—3.3	0.8210	3.36	0.0790	0.9675	58.95
40—48	4.0—4.1	0.6852	4.48	0.1054	1.1325	65.74

#### V Influence of Current quantity.

Anode solution : 2.0 gr. naphthalene  
 100 c.c. acetone  
 50 c.c. H<sub>2</sub>SO<sub>4</sub> (The same concentration as  
 in the previous experiment)

Anode : Lead peroxide

Cathode solution : H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the  
 anode solution)

Cathode : Lead

Current strength : 1.1 ampère

Temperature : 18-23°.

Table VIII.

Current quantity	Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	Material yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone current quantity	Dark brown substance	Oxidizing efficiency
amp. hr.	volt.	gr.	%	%	gr.	gr./amp. hr.	gr.	%
2.53	3.1—3.2	0.8056	3.71	4.61	0.0922	0.0364	0.9942	59.72
5.50	3.0—3.2	0.2784	2.28	6.17	0.1235	0.0224	1.2641	86.08
7.70	3.1—3.3	0.0940	1.94	7.34	0.1468	0.0190	1.4192	95.30

VI Influence of the oxygen carrier.

Anode solution: 3.8 gr. naphthalene  
 100 c.c. acetone  
 50 c.c. H<sub>2</sub>SO<sub>4</sub> (The same concentration as  
 in the previous experiment)  
 1.0 gr. oxygen carrier

Anode: Lead peroxide

Cathode solution: H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the  
 anode solution)

Cathode: Lead

Current strength: 1.1 ampère

Current quantity: 4.73 ampère hours

Temperature: 18–23°.

Table IX.

Oxygen carrier	Voltage	Unchanged naphtha- lene	Current yield of $\alpha$ -naphtho- quinone		Dark brown substance		Oxidizing efficiency	
			volt.	gr.	%	gr.	gr.	%
Vanadic acid.....	2.9—3.1	0.9919	14.98	0.6955	1.9476	73.10		
Chromalum .....	3.1—3.2	1.3136	9.36	0.4347	1.8924	65.43		
Potassium chromate ...	3.0—3.2	1.0662	14.42	0.6694	1.9253	71.93		
Manganese sulphate ...	3.0—3.1	1.2290	12.36	0.5737	1.8767	67.65		
Potassium ferrocyanide.	3.0—3.3	1.2378	11.98	0.5563	1.8416	67.42		
Cobalt sulphate .....	2.9—3.0	1.4376	8.17	0.3794	1.8464	62.16		
Cerium Nitrate .....	3.2—3.3	0.8180	16.29	0.7560	2.0637	78.47		
Mercuric sulphate .....	2.9—3.1	1.2740	10.51	0.4900	1.8717	66.47		
Potassium chlorate ...	3.1—3.2	1.0382	14.80	0.6868	1.9005	72.66		

Anode solution: 2.0 gr. naphthalene  
 100 c.c. acetone  
 50 c.c. H<sub>2</sub>SO<sub>4</sub> (The same concentration as  
 in the previous experiment)  
 1.0 gr. oxygen carrier

Anode: Platinum

Cathode solution: H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the  
 anode solution)

Cathode: Spiral platinum

Current strength: 1.0 ampère

Current quantity: 2.4 ampère hours

Temperature: 40–50°.

Table X.

Oxygen carrier	Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Oxidizing efficiency
			gr.			%
Vanadic acid .....	3.3—3.4	0.4184	9.06	0.2135	1.1823	79.08
Potassium chromate ...	3.2—3.4	0.5128	6.01	0.1502	1.1636	74.36
Cerium sulphate.....	3.2—3.4	0.3652	9.80	0.2308	1.2614	81.74
Potassium chlorate ...	3.1—3.3	0.3972	8.38	0.1976	1.2112	80.14

B. *Electrolytic Oxidation in Sulphuric acid-acetic acid Solution.*

I Influence of concentration of sulphuric acid.

Anode solution: 2.0 gr. naphthalene  
100 gr. glacial acetic acid  
50 c.c.  $H_2SO_4$

Anode: Platinum

Cathode solution:  $H_2SO_4$  (The same concentration as in the anode solution)

Cathode: Spiral platinum

Current strength: 1.0 ampère

Current quantity: 2.4 ampère hours

Temperature: 50–60°.

Table XI.

Concentration of sulphuric acid		Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Oxidizing efficiency
Sulphuric acid	Water						
c.c.	c.c.	volt.	gr.	%	gr.	gr.	%
10	100	3.3—3.4	1.2240	0.93	0.0221	0.6325	38.80
20	100	3.4—3.6	1.1637	1.57	0.0371	0.6687	41.81
30	100	3.2—3.4	1.0760	1.01	0.0240	0.7486	46.20
40	100	3.4—3.6	1.1900	0.43	0.0102	0.6180	40.50
50	100	3.5—3.6	1.3601	0.27	0.0065	0.4833	31.99

II Influence of the current density.

Anode solution: 2.0 gr. naphthalene  
100 c.c. glacial acetic acid  
50 c.c.  $H_2SO_4$  (20 c.c. of  $H_2SO_4$  (sp. gr. 1.84) to 100 c.c. of water)

Anode : Platinum

Cathode solution : H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the anode solution)

Cathode : Spiral platinum

Current quantity : 2.4 ampère hours.

Temperature : 50–60°.

Table XII.

Current strength	Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Oxidizing efficiency
amp.	volt.	gr.	%	gr.	gr.	%
0.5	2.9–3.1	1.0810	0.80	0.0189	0.7268	45.95
1	3.2–3.4	1.0760	1.01	0.0240	0.7486	46.20
1.5	3.9–4.0	1.0452	1.13	0.0267	0.7476	47.74
2	3.8–3.9	1.0200	0.90	0.0212	0.7898	49.00

III Influence of the oxygen carrier.

Anode solution : 2.0 gr. naphthalene

100 c.c. glacial acetic acid

50 c.c. H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the previous experiment)

1.0 gr. oxygen carrier

Anode : Platinum

Cathode solution : H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the anode solution)

Cathode : Spiral platinum

Current strength : 1.0 ampère

Current quantity : 2.4 ampère hours

Temperature : 50–60°.

Table XIII.

Oxygen carrier	Voltage	Unchanged naphthalene	Current yield of $\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Dark brown substance	Oxidizing efficiency
	volt.	gr.	%	gr.	gr.	%
Potassium chromate ...	3.3–3.4	0.6200	3.41	0.0804	1.2705	69.00
Cerium nitrate .....	3.4–3.5	0.5888	3.96	0.0934	1.1679	70.56
Potassium chlorate ...	3.3–3.4	0.6506	3.26	0.0770	1.0935	67.47

III. *The Oxidation Products of Naphthalene*

Ten grams of naphthalene were dissolved in a mixture of 200 c.c. acetone and 50 c.c. of sulphuric acid (20%). Lead peroxide (10×8 cm.) served as the anode and the electrolysis was continued for 26.4 ampère hours with a current of 1.6 ampères. The resultant product was treated in the same manner as in the preliminary experiment.

After separating the yellow crystals which were obtained by the steam distillation, the filtrate was extracted with ether. The ethereal extract was found to contain the  $\alpha$ -naphthoquinone. The ether was cautiously distilled off, and the residue was combined with the yellow crystals. The unchanged naphthalene in the mixture was separated by means of light petroleum ether. The  $\alpha$ -naphthoquinone, which was then recrystallized from the petroleum ether, was obtained in the form of beautiful yellow needles, melting at 125°. The yield was 0.5268 gram. The naphthalene was separated as picrate from the solution in light petroleum ether; the yield was 0.3519 gram.

$\alpha$ -Naphthoquinone isolated as above was analysed with the following results:

0.1935<sup>gr.</sup> substance gave 0.5353<sup>gr.</sup> CO<sub>2</sub> and 0.0641<sup>gr.</sup> H<sub>2</sub>O.

	Found	Cal. (C <sub>10</sub> H <sub>6</sub> O <sub>2</sub> )
Carbon	75.44%	75.93%
Hydrogen	3.70	3.83

After cooling the steam distillation residue and separating from it the dark brown substance, the liquid was extracted with a large quantity of ether. The ethereal extract was decolorized with animal charcoal and the ether was evaporated. A pale brown residue was thus obtained, which was separated by means of the solubility difference, into two components, soluble and insoluble in chloroform.

The part insoluble in chloroform was dissolved in dilute caustic soda solution and again precipitated with hydrochloric acid. After crystallizing from hot water and subjecting it to sublimation it was obtained in white needles. It melted at 128° and was proved, by the fluorescence reaction and by the volumetric analysis according to M. C. Boswell,<sup>(18)</sup> to be phthalic acid anhydride.

To neutralize 0.0324<sup>gr.</sup> substance there was required 4.3 c.c. N/10 NaOH Cal. 0.0318<sup>gr.</sup>.



By evaporating chloroform from the soluble part a pale brown crystalline substance was obtained which was dissolved in hot water. To a portion of this water solution there were added a few drops of ferric chloride, when a brownish blue colouration was produced. Also a dark violet colouration was produced by adding a few drops of bleaching powder. I had thus an evidence of the presence of  $\alpha$ -naphthol by the above colour reactions, but could not isolate it in a crystalline form.

On evaporating another portion of the water solution, a pale brown crystalline substance was isolated. It did not give a definite melting point, although, when dried at  $115^{\circ}$ , it melted at  $144^{\circ}$ , and was proved to be identical with phthalonic acid by a direct comparison with a specimen of that acid prepared by C. Graebe and F. Trümpy.<sup>(19)</sup>

#### IV. *The Dark Brown Oxidation Product*

##### I. Potash fusion.

Three grams of dark brown substance were mixed with 5 c.c. water and 3 grams of potassium hydroxide and heated for 3 hours at  $200$ – $250^{\circ}$  in the oil-bath. After cooling the reaction product was extracted with a large quantity of ether and a considerable quantity of a black insoluble substance was obtained. On distilling off the ether, there remained some white crystals. The crystals were dissolved in caustic soda and reprecipitated with hydrochloric acid and after drying, purified by sublimation. The substance melted at  $128^{\circ}$  and was proved by the fluorescence reaction to be phthalic acid anhydride.

##### II. Oxidation with alkaline potassium permanganate.

Five grams of the dark brown substance were dissolved in a mixture of 7 grams of potassium hydroxide and 400 c.c. water and were warmed with water solution of 40 grams of potassium permanganate for some hours with occasional shaking until the latter was decolorized. When the oxidation was completed, the precipitated manganese dioxide was filtered off. The precipitate was boiled with a large quantity of water, filtered, and pressed. Both the alkaline filtrates were combined under stirring, and were slowly neutralized with concentrated sulphuric acid and evaporated to small volume. It was extracted with ether and, on distilling off ether, some pale brown crystals separated out. The existence of any volatile acid was disproved by the steam distillation,

which gave only a neutral product. On evaporating the distillation residue, a white crystalline substance was obtained which decomposed at  $184^{\circ}$  when recrystallized from hot water. The long white needles obtained by sublimation of this substance, melted at  $128^{\circ}$ . The substance was identified by the fluorescence reaction as phthalic acid anhydride.

Phthalic acid isolated as above was analysed with the following results :

0.2074<sup>gr.</sup> substance gave 0.4371<sup>gr.</sup> CO<sub>2</sub> and 0.0679<sup>gr.</sup> H<sub>2</sub>O.

	Found	Cal. (C <sub>8</sub> H <sub>6</sub> O <sub>4</sub> )
Carbon	57.47%	57.81%
Hydrogen	3.66	3.64

### III. Zinc dust distillation.

Two grams of the dark brown substance were subjected to the zinc dust distillation according to Gattermann's method. The distillation product gave a deep yellow colour with a green fluorescence. It was extracted with a large quantity of benzene, when it gave a yellow substance with yellowish green fluorescence. It was carefully fractionated by means of the difference of solubility in alcohol.

The portion soluble in alcohol was recrystallized with alcohol and its benzene solution was added to the benzene solution of picric acid. When the picrate was purified by recrystallization from benzene, it formed reddish brown needles which melted at  $145^{\circ}$ . Judging from its melting point, it is presumably *αα*-binaphthyl picrate.<sup>(20)</sup>

The part insoluble in alcohol was dissolved in hot benzene, and added to the benzene solution of picric acid. The crystals formed were purified by recrystallization from benzene, when they came out as yellowish brown needles melting at  $184-185^{\circ}$ . After separating picric acid from the substance as ammonium picrate, the picric acid was estimated by E. Feder's method.<sup>(21)</sup> The substance was thus identified as *ββ*-binaphthyl picrate.

0.2213<sup>gr.</sup> substance required 6.2 c.c. of N/10 sodium thiosulphate.

	Found	Cal.
Picric acid	64.11%	64.33%

#### IV. Oxidation with nitric acid.

Three grams of dark brown substance were suspended in 200 c.c. of boiling acetic acid (30%), and 5 c.c. of nitric acid (sp. gr. 1.45) were slowly added with constant stirring. The mixture was heated for a few hours and then the brownish yellow liquid was filtered while hot. A flocky precipitate separated out on cooling. The precipitate and the mother liquor were extracted with ether and then the ether was carefully distilled off. The product thus obtained was distilled with steam and a very small amount of  $\alpha$ -naphthoquinone was found in the distillation. On cooling and filtering the distillation residue, a pale brown crystalline mass was obtained, containing no nitrogen. It was purified by recrystallization from hot alcohol and was found to melt at about 215.5–217°, although the definite melting point was difficult to hit at. Judging by its melting point and its chemical behaviour, it is presumably  $\beta\beta$ -binaphthyl- $\alpha$ -diquinone prepared by F. Chattaway.<sup>(22)</sup> It was oxidized by alkaline potassium permanganate to phthalic acid. In addition to the above substance, I have also obtained a substance insoluble in acetic acid (30%) among the oxidation products with nitric acid. The investigation of this substance is not yet completed.

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