

Electrolytic Reactions of Naphthalene and its Derivatives. Part II. Electrolytic Oxidation of α -Naphthol.

By

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In my previous investigation¹ I qualitatively confirmed the presence of α -naphthol as the intermediate product of the electrolytic oxidation of naphthalene. I have now undertaken to discover the progress of the electrolytic oxidation of α -naphthol, the result of the investigation being reported in the present paper.

According to my experiments, the electrolytic oxidation of α -naphthol takes place only in an acid solution; in an alkaline solution (50 c.c. of 20% sodium hydroxide, 100 c.c. of acetone and 3 grams α -naphthol with platinum electrodes) the formation of α -naphthoquinone could not be observed. As the anode material, platinum, lead-peroxide, nickel and lead were used, of which lead-peroxide gave the best result (Table I). This is due to the higher overvoltage of lead-peroxide on the one hand and its catalytic action on the other. The suitable concentration of sulphuric acid was 10–30%, and especially was the 10% solution found the best (Table 2). The current yield of the first oxidation product was observed to become the smaller the greater the current density, the maximum yield having been attained at about 1 amp./100 sq. cm. (Table 3). The elevation of the electrolytic temperature does not necessarily favour the yield (Table 4). At the beginning of this investigation it was expected that α -naphthoquinone

¹ These memoirs, 5, 111–130, (1921).

would be produced as the chief product as in the case of the electrolytic oxidation of naphthalene, but it was soon found that a beautifully-coloured red compound was first produced, which passed into α -naphthoquinone on further oxidation. I have confirmed this red substance to be the compound of α -naphthol and α -naphthoquinone. As it is evident from table 5, up to about 4 times of the theoretical electric quantity, the increase of the current quantity and of the production of the red compound run parallel. When more current is passed the yield of the red compound decreases and that of the α -naphthoquinone proportionally increases.

It is already known that α -naphthol gives $\alpha\alpha$ -binaphthol by the action of ferric chloride,¹ α -naphthoquinone and phthalic acid by chromic acid² and phthalic acid or phthalonic acid by nitric acid³ or potassium permanganate⁴.

Now by electrolytic oxidation, besides the red compound above mentioned, α -naphthoquinone and phthalic acid, a dark violet substance was always produced. This dark violet substance easily dissolves in boiling alkali, and is precipitated again by acid. It gives a dark blue colouration with ferric chloride. From these facts it may be inferred that the dark violet substance contains the phenolic group in its molecule.

On fusing it with potash it gave a small quantity of phthalic acid, and a larger quantity of phthalic acid and a very small quantity of phthalonic acid were obtained when oxidized with potassium permanganate. By distilling it with zinc dust I have obtained a distillate which dissolves in benzene with an orange yellow colour showing a yellowish green fluorescence. I could also isolate naphthalene and $\alpha\alpha$ -binaphthyl as their picrates from its distillate. From the fact that the dark violet substance gives $\alpha\alpha$ -binaphthyl by the zinc dust distillation and possesses the phenolic property, there is little room for doubting that $\alpha\alpha$ -binaphthol is produced as a step in the oxidation. $\alpha\alpha$ -Binaphthol also gives α -naphthoquinone together with some phthalic acid on further oxidation as may be seen in the experimental parts of this report.

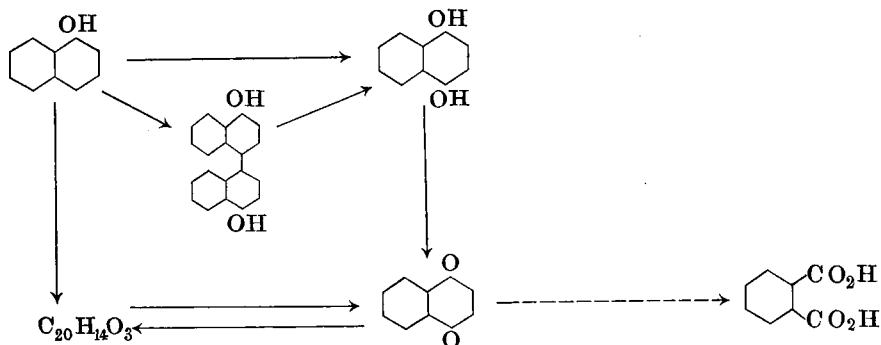
¹ Dianin, J. d. russ. phys. chem. Ges., **6**, 183 (1874); Beilstein's Handb. org. Chem., 1896, **11**, 1004.

² O. Miller, Ber., **14**, 1600 (1881); K. Ono, unpublished.

³ Thorpe, A Dictionary of Applied Chem., 1912, **111**, 615.

⁴ R. Henriques, Ber., **21**, 1608 (1888).

Judging from results so far obtained, I venture to assume that the progress of reaction of the electrolytic oxidation of α -naphthol may be represented by the following scheme :



It is here to be mentioned that the red compound was also formed in the cathode room just as I saw it by the oxidation of naphthalene.

EXPERIMENTAL PART.

α -Naphthol recrystallized from petroleum ether and melting at 96° was used.

(1) PRELIMINARY EXPERIMENT.

There is apparently no record in chemical literature of the electrolytic oxidation of α -naphthol. In order to ascertain what sort of substance is produced by its electrolytic oxidation, the following experiments were performed.

(1) The anode liquid consisting of 100 c.c. of sulphuric acid (10%), 50 c.c. of acetone and 6 grams of α -naphthol 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 covered with lead-peroxide, about 10.0×8.0 cm. served as the cathode. The beaker was cooled with water to keep the temperature of the bath always at about 20° . The

electrolysis was continued for nearly 4.4 ampère hours with a current of 0.8 ampère.

After electrolysis the anode liquid was extracted with ether. The solvent was then evaporated, and the residue subjected to steam distillation. The red crystalline distillate after having been dried was crystallized three times from petroleum ether, and deep red needle crystals, melting at 96–97°, were obtained. It was analyzed by K. H. Meyer's method.

0.1187 grams substance required 7.9 c.c. of N/10 sodium thiosulphate.

	Found	Cal. (C ₁₀ H ₆ O ₂ .C ₁₀ H ₈ O)
<i>α</i> -Naphthoquinone	52.60%	52.31%

From this analytical result it may be inferred that the deep red substance consists of a molecule of *α*-naphthol and of *α*-naphthoquinone. As it dissociates in the organic solvent its molecular weight could not be determined in the usual way. Its solubilities were found as follows :

Solvent	Methyl alcohol	Ethyl alcohol	Amyl alcohol	Acetone	Ether	Chloroform	Carbon bisulphide	Petroleum ether	Acetic acid	Benzene	Toluene	Water
Solubility	soluble	"	"	"	"	"	"	cold—difficult hot—a little	soluble	"	"	cold—very difficult hot—difficult
Colour in solution	yellow	"	"	"	"	"	"	"	"	"	"	"

To separate two components of the red substance from one another the following experiment was performed.

One gram of the red substance was dissolved in a small quantity of hot benzene and a saturated hot benzene solution of picric acid (0.77 gram) was added. On cooling the orange red picrate formed was filtered, washed with a small quantity of carbon bisulphide and dried. Thus about 1.22 grams of the picrate was obtained. Theoretically 1 gram of the substance having composition C₁₀H₆O₂.C₁₀H₈O should give 1.235 grams of naphthol picrate.

The picrate after having been recrystallized twice from alcohol, was found to melt at 189–190° and was proved to be identical with *α*-naphthol picrate by a direct comparison with a pure specimen.

The filtrate from the picrate was distilled, and the residue was

subjected to steam distillation. A nearly quantitative yield of α -naphthoquinone was obtained.

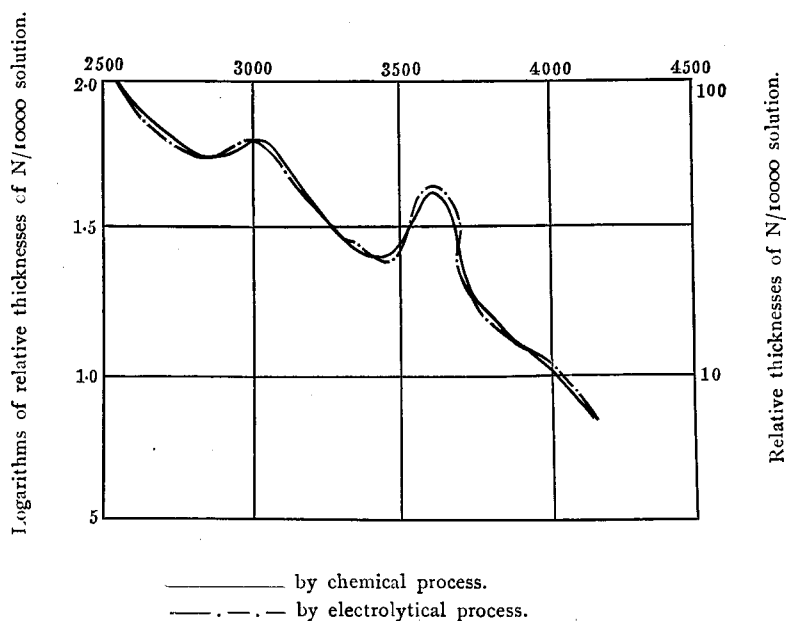
With the object of comparing the red substance electrochemically obtained with α -naphthol- α -naphthoquinone chemically formed I prepared it by mixing the two components in a petroleum ether solution (K. H. Meyer¹). Both are found nearly the same; the only difference observed was their colour, that electrochemically prepared having a deeper tint.

The red substance was analyzed with the following results:

0.1865 grs. substance gave 0.5416 gr. CO₂ and 0.0758 gr. H₂O

	Found	Cal. (C ₂₀ H ₁₄ O ₃)
carbon	79.20%	79.44%
hydrogen	4.54	4.63

For the further confirmation of the identity of the two preparations, spectrographic experiments were conducted according to the well known method of Hartly. For this purpose, their N/10000 solutions were prepared with 20% (vol.) alcohol and a Hilger quartz spectrograph was employed.



¹ Ber., 42, 1153 (1909).

The absorption curve was plotted from the photograph as usual; according to Hartly-Baly's method.¹ As is seen in the figure the curves showing the absorption spectra of the two preparations almost agree with each other, making their identity doubtless.

The anode liquid from which α -naphthol- α -naphthoquinone was distilled off was filtered while hot, and the filtrate was evaporated to a small volume. After dissolving it in a sodium hydroxide solution, the carbon dioxide was passed into the alkaline solution until the phenolic precipitate was no longer formed, and filtered. On acidifying the filtrate, a small quantity of the precipitate separated out, which yielded the long white needles melting at 128° by sublimation. The substance was identified by the fluorescence reaction as phthalic acid anhydride.

(2) In the second experiment the electrolysis was continued for nearly 15.2 ampère hours with a current of 1.6 ampère under the same condition as before. The yellow crystals identified as α -naphthoquinone by the colour reactions with alcoholic phenylhydrazine² and with alcoholic aniline³ was obtained by distilling the anode liquid with steam. It was further characterized as an oxime by heating with hydroxylamine hydrochloride by the method of H. Goldschmidt and H. Schmidt.⁴

Phthalic acid was detected in the residue of the steam distillation.

(II) QUANTITATIVE INVESTIGATION.

Having now confirmed the fact that α -naphthol can be oxidized into α -naphthol- α -naphthoquinone, α -naphthoquinone and phthalic acid, I next attempted to examine the oxidation reaction quantitatively under various conditions. In all experiments I took care to work at a definite current concentration and temperature.

i. Influence of the anode material.

Anode solution: 3.0 gr. α -naphthol
100 c.c. acetone
50 c.c. $H_2SO_4(10\%)$

¹ Baly and Desch, J. Chem. Soc., **85**, 1029 (1904).

² J. Zinck and H. Bindewald, Ber., **17**, 3026 (1884).

³ R. Plimpton, J. Chem. Soc., **37**, 635 (1880).

⁴ Ber., **17**, 2064 (1884).

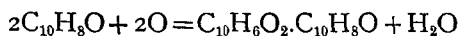
Cathode solution : H₂SO₄(10%)

Temperature : 18–23°.

TABLE I.

Anode		Cathode	Current strength	Voltage	Current quantity	α-naphthol-α-naphthoquinone	α-naphthoquinone	Current yield of α-naphthol-α-naphthoquinone	Material yield of α-naphthol-α-naphthoquinone
Material	Surface area								
Platinum	sq.cm. 40.0	Spiral platinum	amp. 0.8	volt 3.1–3.2	amp.hr. 2.24	gr. 0.4307	gr. 0.2253	% 6.82	% 13.70
Lead peroxide	80.0	Lead	1.6	3.2–3.3	2.24	1.1243	0.5881	17.80	35.75
Nickel	90.0	Nickel	1.8	3.4–3.6	2.25	0.1510	0.0790	2.37	4.80
Lead	80.0	Spiral platinum	1.6	2.8–3.2	2.24	0.3309	0.1731	5.24	10.53

The yield of α-naphthol-α-naphthoquinone was calculated from the value of α-naphthoquinone found analytically, according to the formula (C₁₀H₆O₂.C₁₀H₈O). The current yield was calculated on the assumption that the oxidation takes place according to the following equation :



ii. Influence of the concentration of sulphuric acid.

Anode solution : 3.0 gr. α-naphthol

100 c.c. acetone

50 c.c. H₂SO₄

Anode : Lead peroxide

Cathode solution : H₂SO₄ (The same concentration as in the anode solution)

Cathode : Lead

Current strength : 1.6 ampère

Current quantity : 2.24 ampère hours

Temperature : 18–23°

TABLE II.

Concentration of sulphuric acid	Voltage	α -naphthol- α -naphthoquinone	α -naphthoquinone	Current yield of α -naphthol- α -naphthoquinone	Material yield of α -naphthol- α -naphthoquinone
%	volt	gr.	gr.	%	%
10	3.2-3.3	1.1243	0.5881	17.80	35.75
20	3.5-3.8	0.8386	0.4387	13.28	26.67
30	3.7-4.2	0.7692	0.4023	12.18	24.24
40	4.0-4.4	0.6618	0.3462	10.47	21.05
50	4.3-4.5	0.4624	0.2419	7.32	14.71

iii. Influence of current density.

Anode solution : 3.0 gr. α -naphthol
 100 c.c. acetone
 50 c.c. $H_2SO_4(10\%)$

Anode : Lead peroxide

Cathode : solution : $H_2SO_4(10\%)$

Cathode Lead

Current quantity : 2.24 ampère hours

Temperature : 18-23°.

TABLE III.

Current density	Voltage	α -naphthol- α -naphthoquinone	α -naphthoquinone.	Current yield of α -naphthol- α -naphthoquinone	Material yield of α -naphthol- α -naphthoquinone
amp./100cm. ²	volt	gr.	gr.	%	%
4	4.0-4.3	0.7601	0.3976	12.04	24.18
3	3.5-3.8	0.8356	0.4371	13.23	26.58
2	3.2-3.3	1.1243	0.5881	17.80	35.75
1	2.9-3.1	1.4734	0.7707	23.33	46.87
0.5	2.2-2.5	1.0864	0.5683	17.20	34.56

iv. Influence of electrolytic temperature.

Anode solution : 3.0 gr. α -naphthol
 100 c.c. acetone
 50 c.c. $H_2SO_4(10\%)$

Anode : Lead peroxide
 Cathode solution : H₂SO₄(10%)
 Cathode : Lead
 Current strength : 1.6 ampère
 Current quantity : 2.24 ampère hours

TABLE IV.

Temperature	Voltage	α -naphthol- α -naphthoqui- none	α -naphthoqui- none	Current yield of α -naphthol- α -naphthoqui- none	Material yield of α -naphthol- α -naphthoqui- none
^{°C} 18-23	volt 3.2-3.3	gr. 1.1243	gr. 0.5881	% 17.80	% 35.75
40-53	3.4-3.6	0.7552	0.3952	11.96	24.01

v. Influence of the electric quantity.

Anode solution : 3.0 gr. α -naphthol
 100 c.c. acetone
 50 c.c. H₂SO₄(10%)

Anode : Lead peroxide
 Cathode solution : H₂SO₄(10%)
 Cathode : Lead
 Current density : 0.02 ampère /sq. cm.
 Temperature : 18-23°.

TABLE V.

Current quantity	α -naphthol- α -naphtho- quinone	α -naphtho- quinone	α -naphtho- quinone current quantity	Current yield of α -naph- thol- α -naph- thoquinone	Material yield of α -naph- thol- α -naph- thoquinone	Current yield of α -naphtho- quinone	Material yield of α -naphtho- quinone
amp.hr. 0.56	gr. 0.4231	gr. 0.2213	gr./amp. hr. 0.395	% 26.79	% 13.46	— %	— %
1.12	0.7404	0.3873	0.345	23.44	23.55	—	—
2.24	1.1243	0.5881	0.262	17.80	35.75	—	—
4.48	0.6738	0.7935	0.177	5.33	21.43	6.70	13.36
6.72	0.0893	0.9138	0.135	0.47	2.84	9.20	27.54
8.96	0.0181	0.9477	0.105	0.07	0.57	7.12	29.03
11.20	—	0.8292	0.070	—	—	5.01	25.12

When α -naphthol- α -naphthoquinone and α -naphthoquinone coexisted in the oxidation product, it was first subjected to steam distillation and the distillation product collected in a Gooch crucible, dried and weighed (a). The total amount of α -naphthoquinone was then estimated (b). As (a-b) shows the amount of α -naphthol existing as α -naphthol- α -naphthoquinone the yield of α -naphthol- α -naphthoquinone may easily be calculated.

vi. Influence of the solvent.

In order to know the influence of the solvent on the oxidation, an acetic acid solution (10% sulphuric acid 50 c.c., glacial acetic acid 100 c.c., and α -naphthol 3.0 grs. with platinum electrodes (40 sq. cm.) 0.8 ampère, 2.24 ampère hours) was tried, and as its result only a very small quantity of α -naphthol- α -naphthoquinone and a little larger quantity of phthalic acid were obtained.

(III) OXIDATION PRODUCTS OF α -NAPHTHOL.

Six grams of α -naphthol were dissolved in a mixture of 150 c.c. of acetone and 100 c.c. of sulphuric acid (20%). A sheet of lead covered with lead peroxide, about 10.0 \times 8.0 cm. served as the anode, and the electrolysis was continued for 4.8 ampère hours with a current of 1.6 ampères. The same experiment was repeated three times and the resultant product was treated as in the preliminary experiment. On distilling the product with steam the same red crystalline mass as in the preliminary experiment was obtained. The residue was divided into three parts:

- Part soluble in cold water (A)
- that soluble in hot water (B)
- that insoluble in hot water (C).

Treatment of (A)—(A) was extracted with a large quantity of ether. The brownish red ethereal extract which did not decolorize with animal charcoal was evaporated, and the residue was subjected to fractional distillation.

- (a) 250–275°C reddish oily substance, a little later solidified.
- (b) 275–285°C yellowish oily substance, a little later crystallized.
- (c) residue.

The distillate (a) was pressed on a tile and dark red crystals were obtained. It was recrystallized three times with petroleum ether and formed pale brown crystals, melting at 82–83°. It gave the orange yellow picrate with picric acid, melting at 177–178°.

The distillate (b) which was obtained in the form of brown crystals, was crystallized twice with petroleum ether. It melted at 96° , its picrate melting at $189-190^{\circ}$. They were proved to be identical with α -naphthol and its picrate by a direct comparison with the pure specimens.

After allowing the residue to stand for a few days, a small quantity of colourless needles melting at $184-185^{\circ}$ was separated. A reddish brown colouration followed by precipitation was produced by adding a few drops of ferric chloride, but the fluorescence reaction could not be perceived.

After separating these crystals the residue was dissolved in a caustic soda solution and reprecipitated with hydrochloric acid and the precipitates were sublimed. The sublimed crystals melting at 128° were proved by the fluorescence reaction to be phthalic acid anhydride.

Treatment of (B)—(B) was dissolved in a small quantity of a sodium hydroxide solution, and carbon dioxide was passed into it until the phenolic precipitate was no longer formed, and filtered. The precipitate was treated with diluted mineral acid, dried and extracted with petroleum ether. On distilling off the solvent, the white needles separated out, which was confirmed to be α -naphthol.

The substance insoluble in petroleum ether forms a dark brown picrate, but its further study is not yet concluded.

Treatment of (C)—(C) quite insoluble in boiling water, but soluble in acetone and ether, etc., was easily dissolved by boiling it with alkali from which it was again precipitated by acids. It gave a dark blue colouration with ferric chloride. From these facts it might be inferred that this substance contains the phenolic group. To separate a trace of α -naphthol it was washed with a small quantity of hot benzene and then treated as follows:

(I) POTASH FUSION.

Three grams of this substance were mixed with 5 c.c. of water and 3 grams of potassium hydroxide and heated for 3 hours at $200-250^{\circ}$ in the oil bath. After cooling, the fused mass was dissolved in a little quantity of boiling water, acidified with hydrochloric acid, and filtered. The precipitate was dissolved in a sodium hydroxide solution, and carbon dioxide was passed into it until the phenolic precipitate no longer came out and filtered. A small quantity of the precipitate formed by acidifying the filtrate was dried and sublimed. By

this treatment the long white needles melting at 128° was obtained and confirmed by the fluorescence reaction as phthalic acid anhydride.

(II) OXIDATION WITH POTASSIUM PERMANGANATE.

Two grams of the substance were dissolved in 60 c.c. of 10% sodium hydroxide solution and the solution was warmed with a mixture of 15 grams of potassium permanganate and 250 c.c. of water for some hours with occasional shaking until the solution was decolorized. When the oxidation was completed, the product was strongly acidified with a concentrated sulphuric acid and then evaporated to a small volume. It was extracted with ether, dried and treated with animal charcoal. On distilling off ether, some pale brown crystals separated out. After drying it was dissolved in chloroform, when its greater part remained insoluble. It was dissolved in caustic soda and reprecipitated with hydrochloric acid and, after drying, purified by sublimation. 0.265 gram of a substance melting at 128° and proved to be phthalic acid anhydride by the fluorescence reaction and by a direct comparison with a pure specimen, was obtained.

The part soluble in chloroform when decolorized with animal charcoal was isolated as a pale brown crystalline substance. It was crystallized twice from hot water and dried at 110° . It melted at 144° , and proved to be phthalonic acid.

(III) ZINC DUST DISTILLATION.

Two grams of the substance were subjected to the zinc dust distillation according to Gatterman's method. White crystals were observed to sublime on the wall of the receiver cooled with ice and common salt and at the same time yellow crystals were seen to deposit on the cooler part of the combustion tube.

The white crystals thus obtained had a strong odor of naphthalene. It was confirmed to be naphthalene by examination of its picrate.

The yellow crystals deposited on the cooler part of combustion tube was extracted with a large amount of benzene, when it gave an orange yellow solution with yellowish green fluorescence. The solution was washed with diluted caustic soda solution and evaporated to drive off benzene, when yellow crystals were obtained. It was carefully fractionated into parts soluble and less soluble in alcohol.

The portion soluble in alcohol was recrystallized with alcohol,

and its benzene solution was added to a benzene solution of picric acid. The picrate purified by recrystallisation from benzene, formed reddish brown needles melting at 145°. Judging from this melting point, it is presumably *aa*-binaphthyl picrate.¹

The part with difficulty soluble in alcohol was very small in quantity so that its further examination was impracticable.

(IV) OXIDATION OF *aa*-BINAPHTHOL.

The *aa*-binaphthol used in my experiment was prepared from *α*-naphthol by oxidizing it with ferric chloride according to Morio's² method, and melted at 300–301°.

One gram of *aa*-binaphthol was dissolved in a mixture of 100 c.c. of acetone and 50 c.c. of 10% sulphuric acid. A sheet of lead covered with lead peroxide, about 10.0 × 8.0 cm. served as the anode, and the electrolysis was continued for 5.6 ampère hours with a current of 1.6 ampère.

After electrolysis was over the anode liquid was extracted with ether. The solvent was then evaporated, and the residue was subjected to steam distillation. The distillation product that came out was identified as *α*-naphthoquinone by the colour reactions. It was recrystallized from petroleum ether and was found to melt at 125°. By comparing it with a pure specimen it was proved to be *α*-naphthoquinone. Phthalic acid was detected in the residue of the steam distillation.

(V) OXIDATION OF *α*-NAPHTHOL-*α*-NAPHTHOQUINONE.

One gram of *α*-naphthol-*α*-naphthoquinone which was prepared by electrolysis was dissolved in a mixture of 50 c.c. of acetone and 75 c.c. of 10% sulphuric acid. A sheet of lead covered with lead peroxide, about 10.0 × 8.0 cm. served as the anode and electrolysis was continued for 2 ampère hours with a current of 0.8 ampère.

After electrolysis the anode liquid was extracted with ether. The solvent was then evaporated, and the residue was subjected to steam distillation. The distillation product that came out was identified as *α*-naphthoquinone by the colour reactions. On recrystallizing it from petroleum ether, 0.184 gram of a substance melting at 125° was

¹ H. Walder, Ber., 15, 2171 (1882).

² Unpublished.

obtained and it was proved to be *a*-naphthoquinone. Phthalic acid was also detected in the residue of the steam distillation.

In conclusion, the author wishes to express his sincere thanks to Prof. M. Matsui for his valuable suggestions and kind instructions throughout the work, and to Prof. M. Kimura and Mr. Nakamura for their kind suggestions and advice about the spectrographic experiment and to Mr. Morio for the loan of his unpublished manuscripts.
