

# *Electrolytic Reduction of $\beta$ -Naphthoquinone* (*Reduction of Quinones. II*)

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In the previous paper<sup>(1)</sup> the author has reported the electrolytic reduction of 9,10-phenanthraquinone. This quinone is considerably stable in spite of its being one of the o-quinone but it is supposed that o-quinone are generally unstable.

$\beta$ -Naphthoquinone is one of the o-quinone and is unstable compared with p-quinones; that is, in alcoholic acid solution it is decomposed equimolecular  $\beta$ -naphthohydroquinone and 2-hydroxy-1,4-naphthoquinone.<sup>(2)</sup> It is also transformed into dinaphthyldiquinhydrone slowly in diluted sulfuric acid or rapidly by heating in a sulfuric acid. Therefore, the care must be taken about the treatment of this substance in a acid or alkaline solution.

On the pure chemical reaction  $\beta$ -naphthoquinone is easily reduced to  $\beta$ -naphthohydroquinone with sodium hydrosulfite<sup>(3)</sup>, to 3,4,3',4'-tetrahydroxy-dinaphthyl-(1,1') by heating with zinc chloride in hydrochloric acid solution,<sup>(4)</sup> and to 1,2,4-triacetylnaphthalene in acetic anhydride in the existence of some sulfuric acid.<sup>(5)</sup>

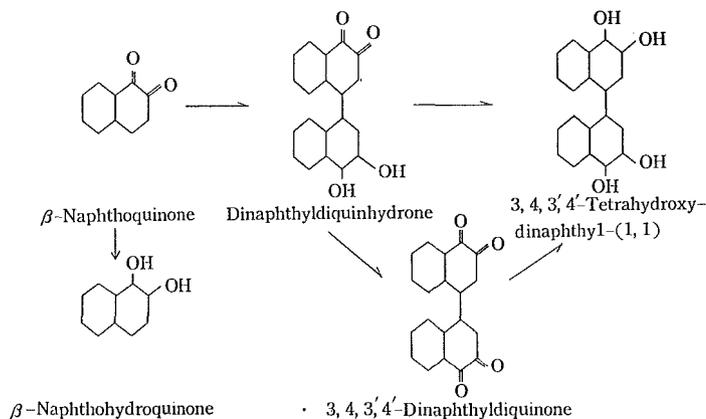
In the present experiment the author tried to see how  $\beta$ -naphthoquinone would act in electrolytic reduction and compare its action with that in the case of pure chemical reaction.

According to the author's experiments,  $\beta$ -naphthoquinone was easily reduced to  $\beta$ -naphthohydroquinone in 60% alcohol solution in the existence of some diluted sulfuric acid. In a sulfuric acid solution, it was easily reduced to dinaphthyldiquinhydrone and this quinhydrone was reduced further to 3,4,3',4'-tetrahydroxydinaphthyl-(1,1').

Dinaphthyldiquinhydrone and tetrahydroxydinaphthyl obtained in the above experiments, were easily oxidized to 1,1'-dinaphthyl-3,4,3',4'-diquinone by nitric acid or bromine water.

Then, it was recognized that this diquinone was reduced to tetrahydroxy-dinaphthyl in alcoholic acid solution.

Moreover, in a electrochemical method the author tried to prepare the other reduction products of  $\beta$ -naphthoquinone, nevertheless other products were not obtained.



### Experimental

$\beta$ -Naphthoquinone used in this experiment, was prepared in the following method<sup>(6)</sup>, that is, orange II was obtained by diazotization of sulfanilic acid and by its reduction 1,2-aminonaphthol was prepared.  $\beta$ -Naphthoquinone was obtained with a good yield by oxidation of 1,2-aminonaphthol with ferric chloride.

#### (I) Reduction of $\beta$ -naphthoquinone to $\beta$ -naphthohydroquinone.

For this purpose electrolysis was conducted under following conditions;  
 Cathode: silver, copper, and nickel plates, 100 cm<sup>2</sup> of area respectively.  
 Cathodic solution: A mixture of 120 ml. of 60% alcohol and some 5% sulfuric acid, in which 2g. of  $\beta$ -naphthoquinone was suspended.

Anode: Pb plate of cylindrical.

Anodic solution: 5% sulfuric acid solution.

Current density: 2 amp./sq. dm..

Time of electrolysis: 2 hours.

Cathodic and anodic solution were separated by unglazed pottery cylinder and the cathodic solution was stirred vigorously. The electrolytic chamber was immersed in a water bath and while solution was kept about 25°C by running water.

After two hours electrolysis the cathodic solution was poured into much water, in which sodium bisulfite had been added to the water beforehand in order to prevent oxidation; then it was extracted with ether and the ether extracts were dried over anhydrous sodium sulfate. The ether was removed at room temperature and the residue was about 1.3g. This was recrystallized twice from the water containing some sulfur dioxide and leaflet crystals were obtained; yield about 0.7g, m. p. 57-59°C.

In order to isolate these crystals as diacetate they were heated with acetyl chloride and recrystallized from water containing sulfur dioxide, m. p. 102–103°C, this corresponds to the diacetate of  $\beta$ -naphthohydroquinone. This hydroquinone was easily oxidized to  $\beta$ -naphthoquinone with 10% ferric chloride solution.

(II) *Reduction of  $\beta$ -naphthoquinone to dinaphthylidiquinhydrone.*

Electrolysis was carried out under following conditions;

Cathode: nickel and silver (100 cm<sup>2</sup> of area).

Cathodic solution: 5% sulfuric acid and alcohol.

Other conditions were the same with (I). As electrolysis advanced, the cathodic solution gradually began to turn green-black from orange and after one hour it became perfectly green-black. This was dinaphthylidiquinhydrone.

Dinaphthylidiquinhydrone was obtained by heating  $\beta$ -naphthoquinone in sulfuric acid (1:2) for ten minutes, but at a low temperature it was not prepared from  $\beta$ -naphthoquinone in 5% sulfuric acid in a short time, therefore, this is regarded as dinaphthylidiquinhydrone due to the combination between reduced  $\beta$ -naphthohydroquinone and  $\beta$ -naphthoquinone.

(III) *Reduction of  $\beta$ -naphthoquinone to tetrahydroxydinaphthyl.*

Electrolysis was carried out under following conditions:

Cathode: nickel and lead plate (100cm<sup>2</sup> of area) and zinc amalgam (15.8cm<sup>2</sup> of area).

Cathodic solution: 30% sulfuric acid and some alcohol or 10% sulfuric acid 60 ml. and 30% acetic acid 60 ml..

Current density: 4 amp./sq. dm.

Time of electrolysis: 1.5 hours.

Temperature: 40–45°C.

Other conditions were the same with (II). As electrolysis advanced, the cathodic solution gradually began to turn greenblack. In that condition electrolysis was going on four hours the electrolyte became light pink colour and the electrolysis was discontinued. This light pink color did not disappear even electrolysis was conducted several hours further.

Foaming of cathodic solution in the case of sulfuric acid was taken off by the addition of alcohol. In a mixture of acetic acid and sulfuric acid, electrolysis was favorable except that the electrolyte became deep colored, therefore it was difficult to find the formation of quinhydrone and the finishing of electrolysis.

The electrolyte was poured into a great deal of water, in which sodium bisulfite had been added to the water beforehand, the solution was stirred sufficiently, then white crystals were deposited. The deposit was filtered off quickly and recrystallized from 30% acetic acid solution containing some sulfur dioxide.

**Table 1** Electrolytic conditions of quinones and reduction products

Expt. No.	Cathode	Catholyte	Temp. °C	c. d. amp./dm. <sup>2</sup>	Time hrs.	Products
(1) <i>β-Naphthoquinone</i>						
1	Ni, Ag, Cu	60% Et-OH 120ml. 5% H <sub>2</sub> SO <sub>4</sub> 10 "	25	2	2	Hydroquinene
2	Ni, Ag	5% H <sub>2</sub> SO <sub>4</sub> 80 " Et-OH 40 "	25	4	0.5	Quinhydrone
3	Ni, Pb	30% H <sub>2</sub> SO <sub>4</sub> 100 " Et-OH 20 "	45	4	1.5	Tetrahydroxy-dinaphthyl
4	"	" "	25	4	3	"
5	Pb	glac. HAc. 60 " 6N-HCl 60 "	25-55	2	4	"
6	Cu, Pb	30% HAc. 100 " 10% H <sub>2</sub> SO <sub>4</sub> 20 "	25	3	4	"
7	Zn-Hg	50% H <sub>2</sub> SO <sub>4</sub> 100 " Et-OH 20 "	60-70	50	7	"
8	Pb, Ni	20%(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 110 " Et-OH 10 "	25	4	5	Blue-black Compound
(2) <i>Dinaphthyl diquinone</i>						
9	Cu, Pb	10% H <sub>2</sub> SO <sub>4</sub> 120 "	25	4	3	Unreduced
10	"	5% H <sub>2</sub> SO <sub>4</sub> 60 " Et-OH 60 "	60	4	3	Tetrahydroxy-dinaphthyl
11	Zn-Hg	50% H <sub>2</sub> SO <sub>4</sub> 60 " glac. HAc. 60 "	90	50	5	"

The yield was 1.5g, m. p. 170-175°C. This was tetrahydroxydinaphthyl. This was added to a mixture of acetic anhydride and sodium acetate and the mixture was heated a little while, and acetylated compounds was obtained, m. p. 155-160°C.

Tetrahydroxydinaphthyl obtained in this experiment and acetylated dinaphthyl had not sharp melting point and was not obtained as clear crystals and the former turned in color to light brown while it was left alone and the color became deep brown gradually.

This reduction product was easily oxidized to dinaphthyldiquinone, orange crystals, by heating with nitric acid or bromine water.

(IV) *Reduction of dinaphthyldiquinone to tetrahydroxydinaphthyl.*

Dinaphthyldiquinone obtained by the oxidation of reduction product in II and III was used in this reduction. Electrolysis was carried out in a mixture of acetic acid and some 10% sulfuric acid, in which 2g. of diquinone was dissolved as diquinone was dissolved easily in acetic acid solution. After finishing the electrolysis the electrolyte was poured into a great deal of water and tetrahydroxydinaphthyl was deposited.

In the case of sulfuric acid only as an electrolyte the reduction did not proceed, but by the addition of alcohol diquinone was reduced easily at a low temperature.

(V) *Reduction of  $\beta$ -naphthoquinone in weak alkaline solution.*

Electrolysis was carried out in a mixture of 20% ammonium sulfate and some alcohol.

Blue-black product was obtained. This substance was not attacked by heating with nitric acid, bromine, and diluted sulfuric acid. Identification of the reduction product was not investigated in this experiment. More detailed studies of this substance will be in progress.

### Summary

Electrolytic reduction of  $\beta$ -naphthoquinone was studied. It was reduced to  $\beta$ -naphthohydroquinone in acidic alcohol solution at a low temperature and it was also reduced to tetrahydroxydinaphthyl in acidic solution by way of dinaphthylidiquinhydrone.

Dinaphthylidiquinone obtained by the oxidation of tetrahydroxydinaphthyl or dinaphthylidiquinhydrone was reduced easily to tetrahydroxydinaphthyl in alcoholic acid solution.

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