

Electrolytic Reduction of Phenanthraquinone

*(Reduction of Quinones I.)**

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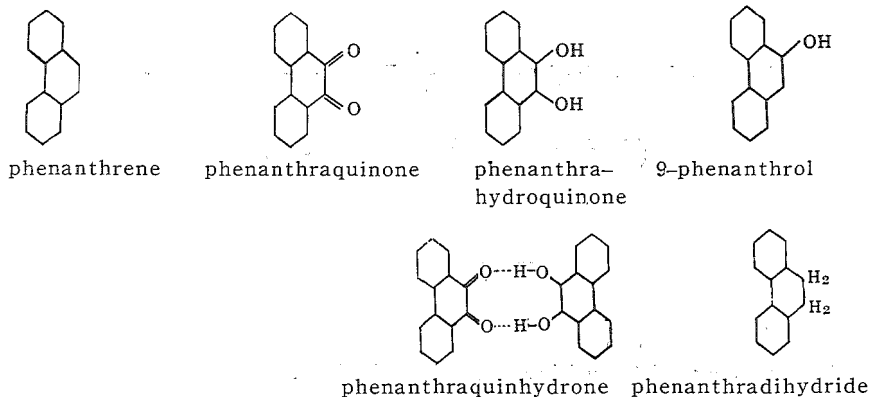
It is supposed that o-quinones are generally unstable compared with p-quinones; but, in view of the specific structure it has been known that 9,10-phenanthraquinone is considerably stable in spite of its being one of the o-quinones and that the quinone behaves in the same way as p-quinones on the pure chemical reaction, it is easily reduced to phenanthrahydroquinone by sulfur dioxide¹⁾ and a kind of reducing agents. It is also reduced to phenanthraquinhydrone by heating with hydrochloric acid in sulfuric acid solution,²⁾ and 9-phenanthrol by heating with a mixture of red phosphorous and hydroiodic acid,³⁾ and by hydrogenation using nickel salts as a catalyst.⁴⁾

In the present experiment the author tried to see how phenanthraquinone would behave in electrolytic reduction and compare its behaviour with that in the case of purely chemical reduction.

According to the author's experiments, phenanthraquinone was easily reduced to phenanthrahydroquinone almost quantitatively in a mixture of diluted sulfuric acid and alcohol at a nickel and copper cathodes, which had a low hydrogen overvoltage. In a mixture of acetic acid and hydrochloric acid solution or a alkaline electrolyte it was found that phenanthraquinhydrone was prepared according to the formation of hydrogen bond between phenanthrahydroquinone and phenanthraquinone.

Moreover, in a electrochemical method the author tried to prepare the complete reduction products of phenanthraquinone; nevertheless, 9-phenanthrol and phenanthradihydride were not obtained by the following experiments, reductions were carried out at a higher temperature in a concentrated acidic electrolyte using lead and zinc amalgam electrodes, and a catalytic reduction by electrolysis was conducted using Raney nickel as a catalyst.

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Experiment and Discussion

Phenanthraquinone was prepared by oxidation of phenanthrene with potassium bichromate in sulfuric acid. This crude products were purified by sodium bisulfite compound and recrystallized from glacial acetic acid. Orange needle crystals were obtained.

(I) Reduction of phenanthraquinone to phenanthrahydroquinone

A. Reduction in acidic solutions

For this purpose electrolysis were conducted under following conditions;

Cathode: Ni, Cu, and Pb plates 100 cm.² respectively; Cathodic solution: A mixture of 60 ml. of 5% sulfuric acid and 60 ml. of alcohol was placed in a porous pot, in which 1 g. of phenanthraquinone was suspended; Anode: Pb plates; Anodic solution: 10% sulfuric acid; Current density: 3 amp./sq. dm. at Ni, Cu, and Pb plates; Time of electrolysis: 1.5 hrs.; Temperature: 60° average.

The electrolytic chamber was immersed in a water bath and while the process of reduction was going on, the temperature of the cathodic solution was kept between 55-65° under stirring. As electrolysis advanced the cathodic solution lost its suspended orange crystals and turned to almost colorless due to the formation of phenanthrahydroquinone, and the decrease in the cathodic solution by evaporation was filled up with alcohol.

After one and half hours the cathodic solution was poured into a great deal of water; then, white crystals were deposited. As the deposit was oxidized quickly in air, sodium sulfite had been added to the water beforehand in order to prevent oxidation. It was filtered quickly and dried under reduced pressure, and it changed in color to light brown while it was being dried. The quantitative yield was obtained, its melting point was 146-149° (not purified).

In order to isolate phenanthrahydroquinone as diacetate the deposit was added to a mixture of acetic acid anhydride and fused sodium acetate and the mixture was heated a little while. This green colored solution was poured into cracked ice. The mixture was allowed to stand and crystals formed were purified by recrystallization from benzene, m.p. 201-202°, this correspond to the reported value of 202° for phenanthrahydroquinone diacetate.

The following factors were investigated on the reduction.

Table

Expt. No.	Cathode	Catholyte	Temp.	c.d.	Time	Product
1	Cu, Ni, Pb	5% H ₂ SO ₄ 60ml. EtOH 60ml.	60°	3	1.5	Hydroquinone
2	Ni	" "	"	1	2.5	"
3	"	" "	"	8	1.0	"
4	"	5% H ₂ SO ₄ 100ml. EtOH 20ml.	"	"	"	Quinhydrone
5	Zn-Hg	30-30% H ₂ SO ₄ 60ml. EtOH 60ml.	"	50	4	Hydroquinone
6	"	" "	25°	50	4	Almost unreduced
7	"	50% H ₂ SO ₄ 60ml. dioxane 60ml.	85°	"	"	Hydroquinone
8	Pb	glac. HAc. 120ml. Na-Acetate 10g.	"	4	"	"
9	"	20% HAc. 120ml. Na-Acetate 10g.	"	"	"	"
10	"	glac. HAc. 70ml. 6N-HCl 70ml.	70°	6	5	Hydroquinone Stand to room temp. Quinhydrone
11	Zn-Hg	glac. HAc. 100ml. 70% H ₂ SO ₄ 20ml.	85°	50	5	"
12	Pb	5% NaOH 60ml. EtOH 60ml.	25°	3	1.5	Quinhydrone
13	"	" "	60°	"	"	" (Green compound)

(i) Nature of the cathodic materials

The reduction products by electrolysis are dependent upon the nature of the cathode materials. As shown in the table, the electrolysis was carried out at various electrodes, nickel and copper which had a low hydrogen overvoltage, and lead and zinc amalgam which had a high hydrogen overvoltage, were used as cathodes. Nevertheless, only phenanthrahydroquinone was obtained in all cases.

(ii) Nature of the cathodic solution

Concerning quantity of alcohol, one-half or more of a cathodic solution was required as shown in expt. 1, because in case of a small quantity of alcohol (expt. 4) phenanthraquinone was refloated or adhered to porous pot and changed in color from orange to black. The black product is regarded as phenanthraquinhydrone due to the formation of hydrogen bond between reduced phenanthrahydroquinone and phenanthraquinone.

When a mixture of dioxane and sulfuric acid was used instead of alcohol at a higher temperature (expt. 7), but similar results also obtained.

S. Ono⁵⁾ studied the electrolytic reduction of anthraquinone and prepared anthraquinol by using various electrodes in a mixture of sodium hydroxide solution and alcohol, anthrone in a mixture of acetic acid and hydrochloric acid solution at a lead cathode, and dihydroanthracene in 80% sulfuric acid at a zinc amalgam electrode.

In the case of phenanthraquinone it has been found that concentration of sulfuric acid between 5% and 80% had no effect on the reduction product. A mixture of acetic acid and hydrochloric acid solution (expt. 10), acetic acid and sulfuric acid (expt. 11), sodium acetate and acetic acid (expt. 9), were used as cathodic solution. Even under these conditions complete reduction products were not prepared.

(iii) Effect of temperature and current density

The temperature was found to influence the reduction velocity. When electrolysis was carried out at 25° average under cooling the chamber with running water (expt. 5), the reduced substance was obtained only partial even after 4 hours, from this it was supposed that the velocity was very slow at a low temperature. It was also found that the current density had no effect between 1 and 8 amp./sq. dm. at a nickel cathode (expt. 1, 2, and 3), but the higher the current density was, the worse was the current efficiency.

In this reduction it was indicated that a high hydrogen overvoltage and a kind of electrolyte at a cathode were not the factors effecting reduction. A low temperature of electrolysis was the sole factor. At a low temperature the following catalytic reduction by electrolysis was effective.

B. Catalytic reduction by electrolysis

Following conditions were thought to be very favorable at a low temperature;

Cathode: Cu and Ni plates 100 cm². ; Cathodic solution: 1 g. of phenanthraquinone was added to a mixture of 60 ml. of alcohol and 60 ml. of 5% sulfuric acid, in which 1 g. of Raney nickel was suspended at the

same time; Temperature: 25° average; Time of electrolysis : 1.5 hrs. Other conditions were the same as given in A. Electrolysis was conducted under stirring. After finishing the supernatant liquid was poured into a great deal of water and phenanthrahydroquinone was obtained.

This was regarded as a catalytic reduction by electrolysis; that is, electrolysis was used only for the evolution of hydrogen.

Furthermore, electrolysis was carried out at a high temperature, other reduction products were not obtained.

(II) Preparation of phenanthraquinhydrone

(i) Reduction in acidic solution

Electrolysis was conducted in a mixture of acetic acid and hydrochloric acid solution to the procedure described in (I) (expt. 10). After finishing the electrolysis cathodic solution was allowed to stand at a room temperature. Shining black needle crystals were isolated, its melting point was 167-168°, and it was oxidized to phenanthraquinone by heating with alcohol. As phenanthrahydroquinone was oxidized in air immediately, it should be oxidized in acetic acid solution and formed phenanthraquinhydrone.

(ii) Reduction in alkaline solution

In a similar manner electrolysis was carried out in a mixture of 60 ml. of 5% sodium hydroxide solution and 60 ml. of alcohol at a lead cathode and carbon anode (expt. 11 and 12).

Phenanthraquinhydrone was the reduction product at a low temperature. The green colored deposit was obtained at a high temperature. The deposit was filtered and gradually turned in color from green to yellow while it was being dried. When this yellow deposit was heated with benzene its color changed to orange, this was phenanthraquinone. When phenanthraquinone was heated with sodium hydroxide solution, its color changed to green. Consequently, it was thought that the green compound was phenanthraquinhydrone.

Summary

Electrolytic reduction of phenanthraquinone was studied. It was reduced to phenanthrahydroquinone or phenanthraquinhydrone.

The catalytic reduction of phenanthraquinone by electrolysis using Raney nickel as a catalyst was thought to be favorable at a low temperature reduction.

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References

1. C.Graebe, *Ann.* 167, 147 (1873)
2. C.Liebermann and P.Jacobson, *Ann.* 211, 69 (1882)
3. F.R.Japp and F.Klingermann, *J.Chem. Soc.* 63, 770 (1925)
4. J.V.Braun and O.Bayer, *Ber.* 58, 2667 (1925)
5. S.Ono, *Bull. of Naniwa Univ.*, 2, Ser. A, 117 (1954)

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