Reduction of Naphthalene by Direct Electrolysis

Akira MISONO, Tetsuo OSA and Takamichi YAMAGISHI

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

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Many polarographic studies of naphthalene have recently been carried out,$^{1)}$ but the reaction products and the reaction conditions in the macro-scale electrolytic reduction of naphthalene have scarcely been investigated at all. Wawzonek *et al.*$^{2)}$ have, however, made experiments on the electrolytic reduction of naphthalene in *N, N*-dimethylformamide. 6.4 g of naphthalene in 150 m*l* of dimethylformamide were electrolyzed for 23 hr by means of a direct current of 0.3—0.05 A, but over 90% of the naphthalene was recorded. Levchenko *et al.*$^{3)}$ reported that dihydronaphthalene was obtained with a current efficiency of 35% in an alkaline solution.

The present authors will examine the reduction of a series of aromatic compounds in various solvents and supporting electrolytes under controlled potential conditions. In the reduction of naphthalene with a very negative reduction potential, 1, 4-dihydronaphthalene was obtained with a good yield with an over 80% current efficiency in an acetonitrile-water solution.

The reaction cell is an H-type cell separated into two chambers with a glass filter. Mercury and platinum are used as cathode and anode respectively. Acetonitrile containing from 5 to 30% water as a proton-donor and tetraethylammonium *p*-toluenesulfonate is used as a solvent. Electrolysis is continued for 8 hr at room temperature. 1, 4-Dihydronaphthalene is identified as follows: water is added to the reaction mixture, and the oily upper layer is separated. The oily products are distilled *in vacuo* after they have been dried with anhydrous sodium carbonate. The fraction (bp 71.8—72.6°C/5 mmHg(uncorrected)) is collected and recrystallized from methanol-water (mp 24.8°C). The IR and NMR spectra of this compound are taken. The reaction products are analyzed by gas chromatography (column, Carbowax 1500 on Diasolid M 2m; column temperature, 180°C; hydrogen carrier gas, 30 cc/min). 1, 2-Dihydronaphthalene and tetralin are confirmed by their retention times in the gas chromatography (5.3 min and 4.1 min respectively). No decalin is detected.

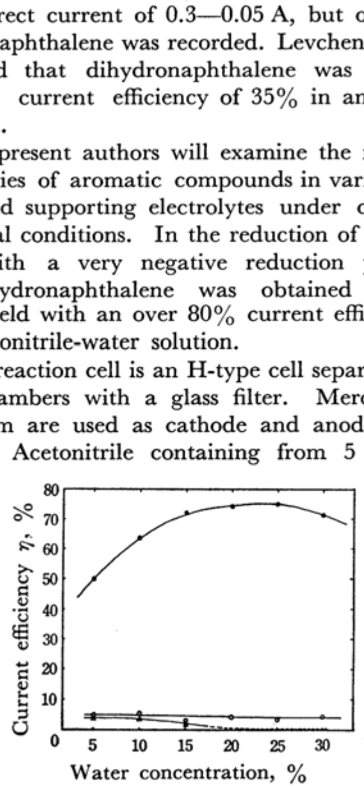

Fig. 1. Effect of water concentration
-●- $\eta_{1.4}$ -▲- $\eta_{1.2}$ -○- η_{Tet}

Figure 1 shows the effect of the water concentration on the current efficiency in a mixture of 10 g of naphthalene and 70 m*l* of acetonitrile-water. The cathode potential is -2.4 V (*vs.* SCE); current, 0.2 A; cathode area, *ca.* 50 cm^2. Upon an increase in the water concentration, the current efficiency of 1, 4-dihydronaphthalene ($\eta_{1.4}$) increases, reaching the maximum value of 75% in a 25% water concentration. On the contrary, the current efficiency of 1, 2-dihydronaphthalene ($\eta_{1.2}$) decreases with an increase in the water concentration and becomes zero in water concentrations of more than 20%. The current efficiency of tetralin (η_{Tet}) is always low and is almost constant.

The best result in 25% aquous acetonitrile solution is obtalned in the mixture containing 8 g of naphthalene and 70 m*l* of the solution with $\eta_{1.4}$ of 83%.

The mechanism of the formation may be supposed to be as follows: at first, the naphthalene molecule accepts one electron from the mercury electrode to form the naphthalene anion radical, and this radical is rapidly protonated by water to form the monohydronaphthalene radical. Next, a one-electron addition occurs at once, without any change in the reduction potential.$^{4)}$ The anion formed is protonated to give 1, 4-dihydronaphthalene.

The detailed results and discussions of the electrolytic reduction of naphthalene and its derivatives will be reported in the near future.

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