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The Selective Reduction of Aromatic Compounds by Electrolysis. I. Reduction of Naphthalene by Electrolysis[1]

Akira MISONO, Tetsuo OSA and Takamichi YAMAGISHI

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

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The direct electro-reduction of naphthalene was investigated in various solvents, mainly in an acetonitrile-water solution using supporting electrolytes containing tetraethylammonium and tetra-*n*-butylammonium cations. The main reduction product was 1,4-dihydronaphthalene, though small amounts of 1,2-dihydronaphthalene and tetralin were also detected. Under optimum conditions, the selectivity and the current efficiency of the formation of 1,4-dihydronaphthalene were 98% and 86.4% respectively. It was found that the water concentration and the solvent had a significant influence on the reduction products and the current efficiency. 1,4-Dihydronaphthalene is mainly formed through the step-by-step addition of two electrons and protons. In addition, 1,4-dihydronaphthalene may be formed by the protonation of the dianion formed by the disproportionation of the anion radical. Further, it was proposed that the formation of the tetraethylammonium radical might partly occur by means of the electron transfer from the anion radical of naphthalene to the tetraethylammonium cation, besides the direct electron transfer to the cation from the electrode.

The reduction of aromatic hydrocarbons by an alkali metal in liquid ammonia or in low-molecular-weight amine, especially in a mixture of liquid ammonia and alcohol (Birch reduction), has been studied by many investigators and a mechanism for the reduction has been proposed.[2] In the electrolytic reduction, many polarographic studies of condensed aromatic hydrocarbons in aprotic solvents in the presence or in the absence of a proton-donor have been reported,[3] but the reduction products and the effect of reaction conditions have scarcely been investigated at all. In regard to the macro-scale electro-reduction of naphthalene, which

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[1] A preliminary announcement of this work appeared in this Bulletin, **40**, 427 (1967).

[2] W. Hückel and H. Bretshneider, *Ann.*, **540**, 157 (1937); A. J. Birch, *Quart. Rev.*, 69 (1950); A. J. Birch and D. Naspuri, *Tetrahedron*, **6**, 148 (1959); A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Scc.*, **81**, 3658 (1959), *etc.*

[3] P. H. Given, *J. Chem. Soc.*, **1958**, 2684; L. H. Klemm and A. J. Kohlik, *J. Org. Chem.*, **28**, 2044 (1963); I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954); S. Wawzonek and E. W. Blaha, *J. Electrochem. Soc.*, **102**, 235 (1955); K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **88**, 2669 (1966), *etc.*

indicates the most negative value in the polarographic half-wave potential among all polycondensed unsubstituted aromatic hydrocarbons, only a few studies have been reported.[4,5] In the reduction of naphthalene by an alkali metal in liquid ammonia or amine, a considerable isomerization of unconjugated products to conjugated compounds occurs, whereas there hardly exists such possibility in the electro-reduction.

The present paper will deal with the macroscale electro-reduction of naphthalene in organic solvents, such as acetonitrile, *N,N*-dimethylformamide (DMF), 1,4-dioxane (DIOX), tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), or diglyme (DGL), in the presence of a proton-donor; the investigation was undertaken in order to clarify the reaction mechanism of the above reaction, to obtain 1,4-dihydro-product selectively, and also to examine the influence of the reaction conditions on the reaction products.

Experimental

Reaction Apparatus. Two different types of cells, H-type and cylindrical cells, with a glass-fritted disk of medium porosity (No. 3 and 4) and of different radii (from 5 to 12 mm) in order to separate the catholyte and anolyte were used. Mercury and platinum were used as the cathode and the anode respectively.

Materials. Naphthalene was purified by recrystallization from methanol - water (mp 79.9—80.0°C). Acetonitrile was purified by distillation from phosphorus pentoxide[6] (bp 81.4°C). DMF was distilled *in vacuo* from calcium oxide (bp 64—65°C/25 mmHg). DIOX and THF were distilled from sodium wire after having been treated with potassium hydroxide[7] (bp 66°C and 101—102°C respectively). DME and DGL were prepared by a variation of the directions in the literature[8] and were purified by distillation from sodium wire[7] (bp 82.5—83.0°C and 162.5—163.0°C respectively). Tetraethylammonium *p*-toluenesulfonate (McKee's salt) was prepared and purified according to the literature.[9] Tetra-*n*-butylammonium bromide was purified by recrystallization from acetone.

Procedure. The base electrolyte was prepared by dissolving a supporting electrolyte in a 100 m*l* solution of a solvent and a proton-donor. This base electrolyte was named, for the sake of convenience, solution A. The catholyte consisted of a substrate to be reduced and 70 m*l* of solution A, while the anolyte was a 30 m*l* portion of solution A. The reaction cell was cooled by a water bath in order to maintain the temperature near room temperature during electrolysis. The cathode potential was set up and controlled by using the saturated calomel electrode (SCE) as a reference electrode and a controlled potential electrolyzer from the Yanagimoto Co., Ltd. (type VE-3). Electrolysis was carried out for about 8 hr with a constant stirring of the catholyte by the use of a magnetic stirrer. The current passed through was measured by a copper coulometer. The variations in the reaction conditions were as follows: water concentration, 0—30 vol%; concentration of the supporting electrolyte, 3—30 g/100 m*l* CH_3CN-H_2O; naphthalene concentration, 6—14 g/100m*l* solution A; cathode potential, from −2.3V to −2.4V *vs.* SCE; current density, 0.05—0.40 A/dm^2; reaction temperature, 2—50°C. The cathode area was about 50 cm^2 in all the experiments.

Identification and Analysis of the Reduction Products. The reduction products were 1,4-dihydronaphthalene (1,4-DHN), 1,2-dihydronaphthalene (1,2-DHN), and tetralin. No further reduction products of naphthalene could be identified.

After the reaction, water was added to the reaction mixture, and the oily upper layer was separated. The oily products were distilled *in vacuo* after having been dried with anhydrous sodium carbonate. The fraction boiling at 71.8—72.6°C/5 mmHg (uncorrected) gave a white crystal (I) (mp 24.8°C) by recrystallization from methanol - water. The reduction products in a THF solution were similarly treated and fractionated to give a fraction boiling at 93.0—93.2°C/19 mmHg. This fraction contained I, another compound, II, which was supposed to be a dihydro-product, and small amounts of naphthalene and tetralin. From the NMR and IR spectra of I, I was identified as 1,4-DHN. By comparing the NMR and IR spectra of the fraction containing II with those of 1,2-DHN prepared from 1,4-DHN by isomerization with sodium isopropoxide in DMF, II was identified as 1,2-DHN. The retention time of II accorded with that of 1,2-DHN in gas chromatography. In NMR spectra, I had absorptions at $\tau=6.65$, 4.11, and 2.94 (intensity ratio 4 : 2 : 4), whereas II had them at $\tau=7.75$, 7.30, 4.15, 3.67, and 3.09 (intensity ratio 2 : 2 : 1 : 1 : 4). In the 1700—1400 cm^{-1} region of the IR spectra, I had absorptions at 1665, 1597, 1590, 1500, 1455, and 1425 cm^{-1}, while II had them at 1600, 1490, 1480, 1450, 1431, and 1420 cm^{-1}. Tetralin was confirmed by the retention time in the gas chromatogram.

The quantitative analysis of the reduction products was performed by the gas chromatographic method (Column, Carbowax 1500 (10%) on Diasolid M (60—80 mesh) 2 m; Column temperature, 180°C; Carrier gas, H_2, 30 cc/min; Detector, Thermal conductivity cell. The calibration of 1,2-DHN was performed with a hydrogen-flame ionizing detector, assuming that the relative molar sensitivities of 1,2- and 1,4-DHN were equal when the hydrogen-flame ionizing detector was used.

The NMR spectra were measured with a JES model LAB-2160 spectrometer (60 Mc), and the IR spectra, with a Hitachi Infrared Spectrophotometer, Model EPI-S2.

Results

Effect of the Reaction Conditions. The electrolytic reduction was mainly carried out in

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[4] S. Wawzonek and D. Wearring, *J. Am. Chem. Soc.*, **81**, 2067 (1959).

[5] V. V. Levchenko and K. V. Meleshko, *Zhur. Obshchei Khim.*, **20**, 831 (1950).

[6] P. Walden, *Z. physik. Chem.*, **144A**, 269 (1929).

[7] "Zikken Kagaku Koza," Vol. 2, Maruzen, Tokyo (1956), p. 82.

[8] J. V. Capinjola, *J. Am. Chem. Soc.*, **67**, 1615 (1945).

[9] M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).

a medium of acetonitrile-water containing McKee's salt as a supporting electrolyte. In the examination of the reaction conditions, the current efficiencies for the formation of dihydro- and tetrahydro-products were defined as follows:

$$\eta_{\mathrm{DH}} = \frac{\text{Amount of the dihydro-product (mole)} \times 2}{\text{Current passage (Faraday)}} \times 100\ (\%)$$

$$\eta_{\mathrm{TH}} = \frac{\text{Amount of the tetrahydro-product (mole)} \times 4}{\text{Current passage (Faraday)}} \times 100\ (\%)$$

In the above equations, the 2 and 4 factors correspond to the numbers of electrons required for the formation of dihydro- and tetrahydro-products respectively.

Effect of the Water Concentration. In the electro-reduction of naphthalene, the concentration of a proton-donor was supposed to be an important factor affecting the reduction products and the current efficiency. The effect of the addition of water as a proton-donor to a solution of tetraethylammonium *p*-toluenesulfonate in acetonitrile was investigated. As is indicated in Fig. 1, the current efficiency was very dependent on the water concentration. As the water concentration increased, the current efficiency for 1,4-DHN ($\eta_{1,4\mathrm{DH}}$) also increased, reaching a maximum value of 74.8% at a 25% water concentration; on the other hand, the current efficiency for 1,2-DHN ($\eta_{1,2\mathrm{DH}}$) decreased with an increase in the addition of water and became almost zero when the water concentration reached 20%. η_{TH} was nearly constant and small except in very low water concentrations. In the electrolysis without water, the catholyte turned dark green and tetralin was formed preferentially, but upon the addition of 5% water no coloration was observed. This color may be due to the anion radical of naphthalene solvated by acetonitrile.

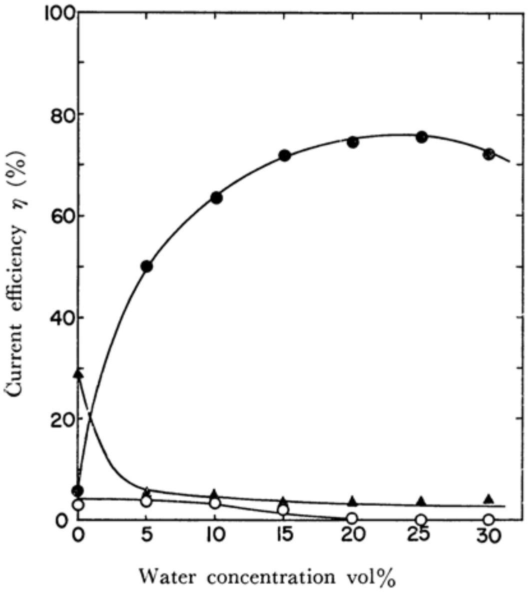


Fig. 1. Effect of the water concentration.
Cathode potential: -2.4 V *vs.* SCE;
McKee's salt concentration: 30 g/100 m*l* CH_3CN-H_2O
Naphthalene Concentration: 14.29 g/100 m*l* solution A
Current density: about 0.35 A/dm^2
—●— $\eta_{1.4\mathrm{DH}}$ —○— $\eta_{1.2\mathrm{DH}}$ —▲— η_{TH}

Effect of the McKee's Salt Concentration. This effect was examined in a 25% water-acetonitrile solution. $\eta_{1,4\mathrm{DH}}$ increased with an increase in the McKee's salt concentration in the low concentration range, but it decreased inversely in the high concentration range. Under the reaction conditions examined, 1,2-DHN was not detected, while η_{TH} remained constant and low (Fig. 2).

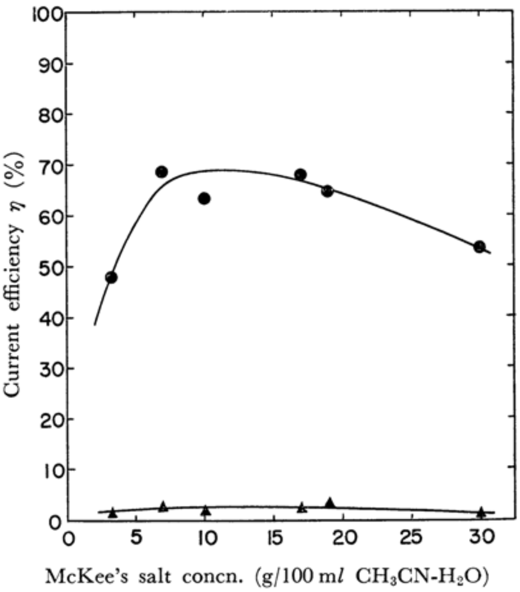


Fig. 2. Effect of the McKee's salt concentration.
Cathode potential: -2.4 V *vs.* SCE;
Water concentration: 25 vol%;
Naphthalene concentration: 11.43 g/100 m*l* solution A;
Current density: about 0.3 A/dm^2.
—●— $\eta_{1.4\mathrm{DH}}$ —▲— η_{TH}

Effect of the Naphthalene Concentration. The effect of the naphthalene concentration is shown in Fig. 3. $\eta_{1,4\mathrm{DH}}$ reached the maximum value of 83% at an optimum naphthalene concentration, but it did not vary much under the conditions examined. η_{TH} remained low and nearly constant. 1,2-DHN was not observed.

Temperature Effect. The reaction temperature was changed over the range from 2 to 50°C. Within this temperature range, $\eta_{1,4\mathrm{DH}}$ increased as the reaction temperature rose (Table 1).

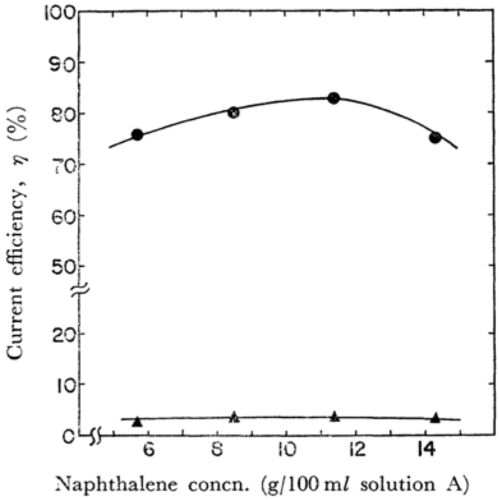


Fig. 3. Effect of the naphthalene concentration.
Cathode potential: −2.4 V *vs.* SCE;
Water concentration: 25 vol%;
Current density: about 0.3 A/dm².
—●— $\eta_{1.4DH}$ —▲— η_{TH}

TABLE 1. TEMPERATURE EFFECT IN THE REDUCTION OF NAPHTHALENE

Temperature (°C)	Reaction time (min)	Current passage (Faraday)	Current density (A/dm²)	$\eta_{1.4DH}$ (%)
2	540	0.0082	0.049	21.4
11	480	0.0119	0.081	37.3
13	460	0.0110	0.078	40.7
30	500	0.0150	0.097	44.2
53	440	0.0266	0.195	55.0

Cathode potential: −2.4 V *vs.* SCE;
Naphthalene concentration: 8.57 g/100 m*l* solution A;
McKee's salt concentration: 20 g/100 m*l* acetonitrile-water;
Water concentration: 20 vol%.

As is shown in Table 1, $\eta_{1,4DH}$ at 30°C was about 1.1 times larger than that at 10°C (both were of approximately same current densities.).

Electrolysis in Various Solvents. The electrolytic reduction of naphthalene was investigated in the following solvents: acetonitrile, DIOX, THF, DME, and DGL. In these experiments, tetra-*n*-butylammonium bromide was used as the supporting electrolyte in place of tetraethylammonium *p*-toluenesulfonate. In an acetonitrile-water medium, $\eta_{1,2DH}$ was low, though it was larger than in an acetonitrile-water-tetraethylammonium *p*-toluenesulfonate system. However, reduction in other solvents (ethers) gave fairly large values of $\eta_{1,2DH}$. η_{TH} was low in all solvents. The ratio of $\eta_{1,2DH}+1/2\eta_{TH}$ to $\eta_{1,4DH}$ was in the following order:

$$\text{DGL} > \text{DME} \approx \text{THF} > \text{DIOX} > \text{Acetonitrile}$$

This order seems to be independent of the dielectric constant of the solvents (Table 2).

Effect of Proton-donors. In the electrolysis, water, methanol, ethanol, phenol, and *p*-hydroxybenzoic acid were used as the proton-donors. The effects of the proton-donors are shown in Table 3. Water, methanol, and ethanol all served as effective proton-donors, though the current efficiency ($\eta_{DH}+\eta_{TH}$) using methanol was a little higher than that using water or ethanol. This result partly depends on the difference in the current density. In the reduction using phenol or *p*-hydroxybenzoic acid as the proton-donor, the main reaction was hydrogen evolution and no formation of dihydro- or tetrahydro-products was observed.

Effect of the Current Density. As shown in Table 3, a large difference was observed in the current efficiencies when methanol was used as the proton-donor. This difference was supposed to be caused mainly by the difference in the current densities. Therefore, we examined the effect of

TABLE 2. SOLVENT EFFECT IN THE REDUCTION OF NAPHTHALENE USING $(C_4H_9)_4NBr$ AS A SUPPORTING ELECTROLYTE

Solvent	CH_3CN	DIOX[a]	THF	DME[b]	DGL[c]
Naphthalene (g/100 m*l*)	11.66	11.66	11.66	11.66	11.66
Reaction time (min)	180	240	180	180	180
Current passage (Faraday)	0.0083	0.0096	0.0201	0.0272	0.0199
$\eta_{1.4DH}$ (%)	27.9	43.0	43.6	49.5	38.8
$\eta_{1.2DH}$ (%)	7.4	22.9	26.8	30.3	34.8
η_{TH} (%)	—	—	6.1	4.5	2.9
$\frac{\eta_{1.2DH}+\frac{1}{2}\eta_{TH}}{\eta_{1.4DH}}$	0.27	0.53	0.68	0.66	0.94
Dielectric constant	37.5 (20°C)	2.209 (25°C)	7.39 (25°C)		7 (20°C)

Cathode potential: −2.4 V *vs.* SCE;
Water concentration: 12.5 vol%;
Reaction temperature: 20—24°C
$(C_4H_9)_4NBr$ concentration: 15 g/100 m*l* solution A.
a) Dioxane. b) 1,2-Dimethoxyethane. c) Diglyme.

TABLE 3. EFFECT OF THE PROTON-DONOR IN THE REDUCTION OF NAPHTHALENE

Proton-donor	Concentration (mol/l)	A/dm^2	$\eta_{DH}+\eta_{TH}$ (%)	pK_a
Phenol[a)]	6.22	0.10	0	9.9
p-Hydroxybenzoic acid[b)]	3.22	0.22	0	13.8
Water[b)]	3.22	0.37	66	14
Water[a)]	6.22	0.21	68	
Methanol[b)]	3.22	0.40	71	16
Methanol[a)]	6.22	0.10	47	
Ethanol[b)]	3.22	0.28	58	18
Acetonitrile[a)]		0.12	38	25
Water[c)]	13.99	0.14	52	

a) Cathode potential: -2.4 V *vs.* SCE; Naphthalene concentration: 8.57 g/100 ml solution A; McKee's salt concentration: 20 g/100 ml acetonitrile-water.
b) Cathode potential: -2.3 V *vs.* SCE; Naphthalene concentration: 11.43 g/100 ml Solution A; McKee's salt concentration: 22.2 g/100 ml acetonitrile-water.
c) *N,N*-Dimethylformamide was used as a solvent instead of acetonitrile, other conditions were the same as a).

TABLE 4. EFFECT OF CURRENT DENSITY

Current density (A/dm^2)	Reaction time (min)	Current passage (Faraday)	$\eta_{1,4DH}$ (%)	η_{TH} (%)
0.08	420	0.0110	46.1	2.3
0.13	300	0.0118	49.2	1.0
0.17	480	0.0258	74.2	3.5
0.68	180	0.0380	86.2	2.3
0.78	200	0.0483	86.4	2.8

Cathode potential: -2.3 V *vs.* SCE; Naphthalene concentration: 11.43 g/100 ml solution A; McKee's salt concentration: 30 g/100 ml acetonitrile-water; Water concentration: 20 vol%.

the current density by altering the porosity and radius of the glass-fritted disk[*1] (Table 4). It was observed that $\eta_{1,4DH}$ increased with an increase in the current density, while η_{TH} did not vary much. Therefore, the ratio of $\eta_{1,4DH}$ to η_{TH} increased with an increase in the current density.

Discussion

Among the reaction factors examined, the water concentration and the solvent showed the most considerable influence on the reduction of naphthalene.

The measurement of the polarogram of naphthalene has shown that the first reduction wave involves only one one-electron addition, while the next one-electron addition occurs at a more negative potential in an aprotic system.[10] In the presence of a proton-donor, the anion radical is immediately protonated to become a monohydro radical. As the reduction potential of this monohydro radical is more positive than that of the original molecule,[11] the one-electron addition that follows occurs easily, without any change in the reduction potential, and a two-electrons transfer wave is observed. Therefore, in a reduction with an unsufficient amount of a proton-donor, the current efficiency of 1,4-DHN will be low. The tendency shown in Fig. 1 was consistent with this prediction, though the behavior of η_{TH} was in contrast with that of $\eta_{1,4DH}$. In the presence of a large amount of water, the solubility of naphthalene lowered and a considerable evolution of hydrogen occurred; thus $\eta_{1,4DH}$ had a maximum value under optimum conditions when the addition of water increased.

As has been mentioned previously, during the reduction of naphthalene in the medium of anhydrous acetonitrile, the catholyte turned dark green and the overall current efficiency was low. A considerable amount of the anion radical may take the following possible courses prior to protonation in the absence of water, for acetonitrile is not such an effective proton-donor as water, ethanol, or methanol:

1. Dimerization of anion radicals.
2. Electron transfer to a tetraethylammonium cation.
3. Electron exchange with an electrode.

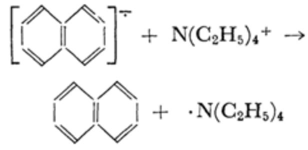
If the dimerization of the anion radicals occurs, 1,4,1′,4′-tetrahydro-1,1′-binaphthalene will be formed. The naphthalene consumed was, however, almost entirely converted to the monomeric reduction products and no dimeric products could be detected. Therefore, the dimerization of the anion radicals is regarded as negligible.

[*1] The current density was changed fairly much by this means, but the cathode potential could not be maintained at the set potential for long (for a few hours in the extreme case) after the reaction started in electolyses with low current densities.

10) P. H. Given and M. E. Peover, *J. Chem. Soc.*, **1960**, 385.

11) G. J. Hoijtink, J. van Schooten, E. de Boer and W. Ij. Aalbersberg, *Rec. Trav. Chim.*, **73**, 355 (1954).

If the electron transfer to a tetraethylammonium cation takes place, the tetraethylammonium radical will be formed. This radical, being unstable, decomposes into triethylamine and ethyl radical.[12] The gas-chromatographic analysis of the gaseous products of the electrolysis of naphthalene in anhydrous acetonitrile containing tetraethylammonium *p*-toluenesulfonate indicated that the gaseous products contained a considerable amount of C_2H_4 and a small amount of C_2H_6 (the ratio of C_2H_4 to C_2H_6 was about 30 : 1, and the current efficiency for $C_2H_4+C_2H_6$, about 30%). The tetraethylammonium radical is also formed by the direct electron transfer to the tetraethylammonium cation from the electrode.[13] The polarographic analysis of naphthalene in anhydrous acetonitrile-tetraethylammonium *p*-toluenesulfonate showed that naphthalene was reduced at about 0.25 V more anodic potential than the cation of the supporting salt. Accordingly, the following process may be included in the reaction scheme besides the direct electron transfer to the tetraethylammonium cation:

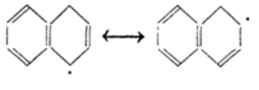


$$\cdot N(C_2H_5)_4 \rightarrow N(C_2H_5)_3 + \cdot C_2H_5$$

In Table 2, the ratios of $\eta_{1,2\rm DH}+\frac{1}{2}\eta_{\rm TH}$ to $\eta_{1,4\rm DH}$ for the solvent used increase in the following order:

DGL > DME ≈ THF > DIOX > Acetonitrile

The order of the ethers was consistent with the basicity of the ethers as Lewis bases. The above order may be supposed to represent the solvation effect on the anion radical or the monohydro radical of naphthalene by the solvents used. The anion radical of naphthalene may be tentatively shown as below:



As the basicity of the solvent increases, the electronic configuration of the naphthalene anion radical solvated will be changed and the electron density of the 2 position may increase. A similar change will occur with the monohydro radical of naphthalene. Therefore, the formation of 1,2-DHN will increase as the basicity of the solvent increases in the cases of ether solvents.

In Fig. 1, the behavior of $\eta_{\rm TH}$ is remarkable. $\eta_{\rm TH}$ has a value of 29.3% when the water concentration is 0%. This predominant formation of tetralin in anhydrous acetonitrile can be similarly ascribed to the change in the electronic configuration of the naphthalene radical, brought about by the solvation by acetonitrile. This change results in the preferential formation of 1,2-DHN, which is then easily reduced to tetralin as the polarographic half-wave potential of 1,2-DHN is nearly the same as that of naphthalene (though it is slightly more negative than that of naphthalene).[14] The addition of water will change the solvation by acetonitrile and will cause 1,4-DHN to be preferentially formed.

The solvation state cannot be simply interpreted by the apparent physical properties of the solvent, such as its basicity as a Lewis base, its dielectric constant, and so on. We intend, therefore, to clarify the solvent effect by utilizing the ESR technique.

The effect of the concentration of McKee's salt can be interpreted as the coexistence of the stabilization of the naphthalene anion radical by the tetraethylammonium cation and the electron transfer to the cation from the anion radical. At a low concentration of McKee's salt, the stabilization effect is predominant, but with an increase in the concentration the electron transfer may increase. Furthermore, the approach of the water molecule may be hindered by the bulky tetraethylammonium cation.

The rise of the reaction temperature seems to accelerate the protonation of the anion radical by water and relatively suppress the side reactions of the anion radical within the temperature range examined.

As may be seen in Table 3, the values of $\eta_{\rm DH}+\eta_{\rm TH}$ were not very different when water or methanol was used as a proton-donor with fairly high current densities over about 0.3 A/dm^2. The dissociation constants of water and methanol are, however, different. In the case of ethanol, $\eta_{\rm DH}+\eta_{\rm TH}$ had a fairly large value (52%). Furthermore, in the medium of acetonitrile without water, the sum of the current efficiencies was about 38%, not much less than what we had expected from the dissociation constant of acetonitrile if the protonation was mainly the addition of a free proton to the anion radical or to the monoanion. In the reduction using phenol or *p*-hydroxybenzoic acid as a proton-donor, 1,4-DHN was not formed and the evolution of hydrogen occurred predominantly. Therefore, the protonation of the naphthalene anion radical and monoanion occurred mainly by the abstraction of the proton from the proton-donor, as has been proposed on the basis of the results of

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[12] H. H. Schlubach, *Ber.*, **53B**, 1689 (1920).

[13] M. Finkelstein, R. C. Petersen and S. D. Ross, *J. Am. Chem. Soc.*, **81**, 2361 (1959); S. D. Ross, M. Finkelstein and R. C. Petersen, *ibid.*, **82**, 1582 (1960); M. Finkelstein, *J. Org. Chem.*, **27**, 4076 (1962).

[14] S. Wawzonek and H. A. Laitinen, *J. Am. Chem. Soc.*, **64**, 2365 (1942).

the polarographic studies,[10,15] though a part of the protonation may occur by the addition of a free proton to the anion. The fact that phenol or *p*-hydroxybenzoic acid did not serve as the proton-donor indicates that the hydrogen atom scarcely contributed at all to the reduction of naphthalene.

It is obvious that the reaction proceeds in accordance with the following reaction scheme:

$$\begin{aligned}
&\mathrm{R} + \mathrm{e} \rightleftarrows \mathrm{R}^{\cdot-} \\
&\mathrm{R}^{\cdot-} + \mathrm{HX} \rightarrow \cdot\mathrm{RH} + \mathrm{X}^- \\
&\cdot\mathrm{RH} + \mathrm{e} \rightarrow \mathrm{RH}^- \\
&\mathrm{RH}^- + \mathrm{HX} \rightarrow \mathrm{RH}_2 + \mathrm{X}^-
\end{aligned}$$

where HX is the proton-donor. Further, as shown in Table 4, a tendency for $\eta_{1,4\mathrm{DH}}$ to increase with an increase in the current density was observed. Therefore, it may be supposed that this equilibrium may exist:

$$2\mathrm{R}^{\cdot-} \rightleftarrows \mathrm{R}^{2-} + \mathrm{R}$$

The increase in the current density may result in an increase in R^{2-}, thus suppressing the side reactions of $\mathrm{R}^{\cdot-}$ (as the proton affinity of a dianion is larger than that of an anion radical) and increasing the current efficiency for 1,4-DHN formation. As has been described before, the naphthalene consumed was exclusively converted to the monomeric hydrogenated products, and the proportion of the dimerization of anion radicals was small.

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15) S. Wawzonek and J. W. Fan, *ibid.*, **68**, 2541 (1946).