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Electrolytic Reduction of Naphthalene in Various Alcohol-Hexamethylphosphoramide Systems

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The electrolytic reduction of naphthalene was carried out in various alcohol-hexamethylphosphoramide (HMPA) systems in the presence of lithium chloride. The reduction of naphthalene proceeds effectively at relatively low cathode potentials in the presence of HMPA; the composition of the products varies with the changes in the reduction potential, the kind of alcohols, and the concentration of HMPA. The dark blue color is observed at the cathode during the electrolysis in HMPA solutions in either the presence or the absence of ethanol. It is suggested that the color reflects the generation of solvated electrons, and that reduction of naphthalene is caused not through a direct electron-transfer from the cathode, but through a reaction with solvated electrons as the reductive agent.

In this series of investigations, the reduction of various organic compounds by solvated electrons will be discussed. It has been considered that the solvated electrons are generated especially in polar solvents by high-energy radiation and exist in amine or ether solutions of alkali metals, especially in a dilute metal-ammonia solutions.1) Extensive investigations have been carried out into their properties and reactions with various compounds in metal-ammonia solutions; however, there have been few investigations of reactions in other systems.2,3) The existence and the properties of solvated electrons have been suggested and examined by the methods of electric conductivities, absorption spectra, and electron-spin resonances, but a complete understanding has not yet been obtained. Recently, Sternberg *et al.* reported a series of investigations of the electrolytic reduction of aromatic compounds in the ethylenediamine-lithium chloride systems and suggested that the reduction was caused by an indirect electron-transfer mechanism.4,5) In these systems, it might be considered that the solvated electrons act as a reductive agent. In the present paper, the electrolytic selective reduction of naphthalene in mixed solvent systems of various alcohols and hexamethylphosphoramide in the presence of lithium chloride will be reported. The generation of solvated electrons has been suggested in this system.6)

Experimental

Reagents. The hexamethylphosphoramide (HMPA, Japan Oil Seal Co.) was purified by reflux over calcium hydride and by subsequent distillation under reduced pressures. The alcohols (methanol, ethanol, 1-propanol, and 2-propanol) were purified by reflux over calcium oxide and by distillation. Lithium chloride of a reagent grade was used without further purification, while the naphthalene was purified by recrystallization and sublimation.

Apparatus and Procedure. The electrolysis vessel used is an H-cell with a total capacity of 40 m*l*. It is separated by a filter paper, Toyo Roshi No. 2, into two compartments. A platinum anode and cathode were used through the present experiments. The area of each electrode is 3 cm^2. The electrode potential was measured against an Ag wire used as a reference electrode. The electrolysis vessel was set in a water bath maintained at nearly constant temperatures, 18—20°C. All electrolyses were carried out at constant voltages or constant currents by a manually-controlled device.

The concentrations of naphthalene and lithium chloride are 0.2 and 0.5 M respectively, except when otherwise stated; the total volume of the reaction mixture is 20 m*l*, and the HMPA content varies from 0 to 50 vol%.

The reduction products were analyzed by gas chromatography (column, polyethylene glycol 6000, 2.5 m; column temperature, 150°C; helium flow rate, 40 m*l*/min) and by mass-spectrometry. The identification was made through a comparison of the retention time with those of the authentic samples, while the yield was estimated by the measurement of the peak heights.

Results

Ethanol-HMPA System. The results for the electrolysis of naphthalene in a mixed ethanol-HMPA system containing lithium chloride are

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1) "Solvated Electron," Adv. Chem. Ser., 50 (1965).

2) M. C. R. Symons, *Quart. Rev.* (*London*), **13**, 99 (1959).

3) M. J. Sienko and G. Lepoutre, eds., "Metal-Ammonia Solutions," Benjamin, New York (1964).

4) H. W. Sternberg, R. E. Markby and I. Wender, *J. Electrochem. Soc.*, **110**, 452 (1963).

5) H. W. Sternberg, R. E. Markby and I. Wender, *ibid.*, **113**, 1060 (1066).

6) H. W. Strernberg, R. E. Markby and I. Wender, *J. Am. Chem. Soc.*, **89**, 186 (1967).

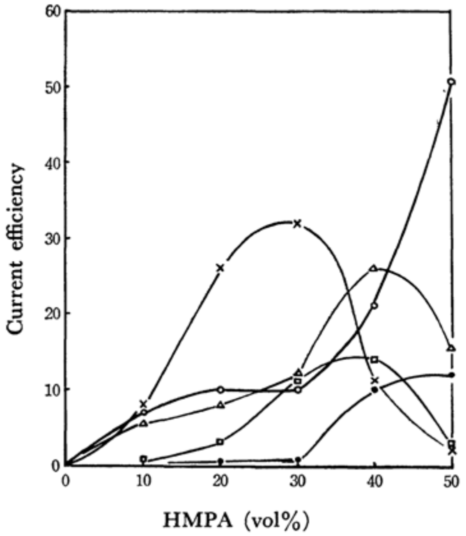

Fig. 1. Ethanol-HMPA system at −3.10 V *vs.* Ag wire.
○—○ Dihydronaphthalene ●—● Tetralin
△—△ Hexaline □—□ Octalin
×—× Decalin

given in Fig. 1. The concentrations of naphthalene and lithium chloride were 0.4 and 0.5M, respectively, and the cathode potential was maintained at nearly −3.10 V *vs.* Ag wire. This potential is more negative by about 1 volt than the reduction potential of naphthalene. As is shown in Fig. 1, no reduction products were detected in the absence of HMPA. When HMPA is added, the reduction of naphthalene occurs effectively, and the total current efficiency for the production of hydronaphthalenes increases with an increase in the HMPA content. The selectivity of reduction depends remarkably on the HMPA content. The current efficiencies for dihydronaphthalenes and tetralin increase monotonously with an increase in the content of HMPA, ranging from 0 to 50 vol%; on the other hand, the maximum current efficiencies of hexalin, octalin, and decalin are found at 40, 35, and 30 vol% of HMPA, respectively.

The electrolytic reduction at various reduction potentials was carried out under similar conditions.

TABLE 1. ELECTROLYTIC REDUCTION OF NAPHTHALENE IN ETHANOL-HMPA SYSTEM AT −1.70±0.05 V *vs.* Ag WIRE

HMPA (vol%) Product (mole ratio, %)	40	30	20	10
1,2-Dihydronaphthalene	12	—	34	33
1,4-Dihydronaphthalene	88	100	66	67
Curr. eff. (%)	61.3	50.4	44.0	25.2

Table 1 shows the results of electrolytic reduction at −1.7±0.05 V *vs.* Ag wire. The reduction products are 1,2- and 1,4-dihydronaphthalene, with the latter the main product. The electrolyses carried out at −2.0±0.05 V and −2.5±0.05 V *vs.* Ag wire also afford only 1,2- and 1,4-dihydronaphthalene.

Methanol-HMPA System. In order to get some insights into the effect of alcohols on the reduction of naphthalene, the electrolytic reduction was carried out in the methanol-HMPA system under conditions similar to those in the ethanol-HMPA system. The results are shown in Tables 2 and 3.

TABLE 2. ELECTROLYTIC REDUCTION OF NAPHTHALENE IN METHANOL-HMPA SYSTEM AT −1.20—−1.30 V *vs.* Ag WIRE

HMPA (vol%) Product (mole ratio, %)	40	30	20	10
1,4-Dihydronaphthalene	100	100	88	64
Tetralin	—	—	12	36
Curr. eff. (%)	8.2	15.3	16.1	26.2

TABLE 3. ELECTROLYTIC REDUCTION OF NAPHTHALENE IN METHANOL-HMPA SYSTEM AT −1.70—−1.75 V *vs.* Ag WIRE

HMPA (vol%) Product (mole ratio, %)	50	40	30	20	10
1,4-Dihydronaphthalene	88	90	83	82	82
Tetralin	6	10	16	18	18
Hexalin	6	—	1	—	—
Curr. eff. (%)	85.3	38.8	40.8	27.1	20.1

In the absence of HMPA, the reduction of naphthalene does not occur. When HMPA is added, the main products are dihydronaphthalenes and tetralin, but the yield of tetralin decreases with an increase in the HMPA content. The selective reduction into dihydronaphthalenes becomes almost complete at higher HMPA contents, especially when the electrode potential is low. The total current efficiency increases with an increase in the content of HMPA, except for the case of a lower electrode potential (−1.20—−1.30 V *vs.* Ag wire). Table 4 shows the effect of the cathode potential in the range from −1.20 to −1.75 V *vs.* Ag wire at the HMPA content of 30 vol%. The increase in reduction potentials results in an increase in the total current efficiency, but a decrease in the selectivity for the formation of dihydronaphthalenes.

It must be noticed that the electrolytic reduction of naphthalene takes place steadily at the cathode potential of −1.20—−1.30 V *vs.* Ag wire. The polarographic half-wave potential of naphthalene

Table 4. Effect of cathode potentials on reduction of naphthalene in methanol-HMPA system (HMPA content 30 vol%)

Cathode potential V *vs.* Ag wire	Product (mole ratio, %)			Curr. eff. (%)
	1,4-Dihydronaphthalene	Tetralin	Hexalin	
−1.25±0.05	100	—	—	15.3
−1.52±0.03	82	18	—	35.3
−1.72±0.03	83	16	1	40.8

Table 5. Electrolytic reduction of naphthalene in 2-propanol-HMPA system under constant current 20 mA (Total electricity 190 coul.)

HMPA (vol%) Porduct (mole ratio, %)	30	20	10	0
1,2-Dihydronaphthalene	90	84	63	70
1,4-Dihydronaphthalene	3	5	15	15
Tetralin	7	8	11	10
Hexaln	—	3	11	5
Curr. eff. (%)	100	92	92	50
Cathode potential (V *vs.* Ag wire)	3.5—4.2	6.4—7.0	10—20	40—60*

* This value is very irreproducible.

Table 6. Electrolytic reduction of naphthalene in 2-propanol-HMPA system under constant current 20 mA (Total electricity 190 coul.)

HMPA (vol%) Product (mole ratio, %)	30	20	10	0
Dihydronaphthalene	2	—	—	100
Tetralin	5	5	—	—
Hexalin	9	10	12	—
Octalin	4	—	—	—
Decalin	80	85	88	—
Curr. eff. (%)	100	100	100	10
Cathode potential (V *vs.* Ag wire)	4.9—5.5	6.0—10	6.0—7.8	50—60*

* This value is very irreproducible.

has been reported to be −1.98 V *vs.* SCE in an ethylene glycol monomethyl ether solution using 0.1 M tetrabutylammonium iodide as a supporting electrolyte,7) and −2.53 V *vs.* SCE in a 75% dioxane solution.8) Even if the reduction potential in the macro-electrolysis differs somewhat from that in micro-electrolysis, this finding shows that the electrolytic reduction of naphthalene does occur in a system containing HMPA at lower cathode potentials than the half-wave potential, which is required for the direct electron-transfer from the cathode to naphthalene molecules. This fact may be interpreted on the assumption of some indirect electron-transfer machamism, which is probably closely connected with the existence of HMPA, as will be discussed in detail later.

Propanol-HMPA System. In order to examine the effect of alcohols further investigations were carried out by using 2-propanol and 1-propanol. The electrolysis was done under a constant current of 20 mA, because these systems are very resistive and a sufficiently high current is not obtained when a similar cathode potential as employed in the methanol and ethanol system is used. The results in the 2-propanol-HMPA system are shown in Table 5, where the cathode potentials are also given. Upon an increase in the HMPA content, the cathode potential decreases remarkably. In the absence of HMPA, the cathode potential is irreproducible but very high, and naphthalene is reduced electrolytically into hydronaphthalenes; this is in contrast to the case of a pure methanol or ethanol system, where a high-electrode potential sufficiency for direct electron-transfer is not retained.

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7) E. M. Elofson, *Anal. Chem.*, **21**, 916 (1949).
8) G. J. Hojitink and J. V. Schooten, *Rec. Trav. Chim.*, **71**, 1089 (1952).

The results of electrolyses in the mixed solvents of 1-propanol-HMPA are shown in Table 6. In the absence of HMPA, the cathode potential is very high and naphthalene is reduced into dihydronaphthalenes electrolytically, but the current efficiency is very low. Upon an increase in the HMPA content, the cathode potential necessary for the passage of a constant current, 20 mA, decreases, but the total current efficiency for the reduction of naphthalene is nearly quantitative and the main product is decalin.

Effect of the Addition of Water. In order to examine the effect of the addition of water as a proton donor, the electrolysis of naphthalene in the ethanol-HMPA-water system (volume ratio, 10 : 10 : 4) was carried out. The conditions of electrolysis were as follows: the concentration of naphthalene and LiCl are 0.32 M and 0.4 M, respectively, and the cathode potential is 3.0 V *vs.* Ag wire. During the electrolysis the evolution of gas is violent at the cathode, probably because of the electrolytic decomposition of water, but naphthalene is not reduced on the passage of 4.68×10^2 coulomb.

Current-Voltage Relation. In Fig. 2 the current-voltage relationships in systems of water, methanol, ethanol, 1-propanol, 2-propanol, and respective alcohol-HMPA mixed solvents containing 0.5 M lithium chloride are shown. The cell temperature was maintained at 18—20°C in a water bath.

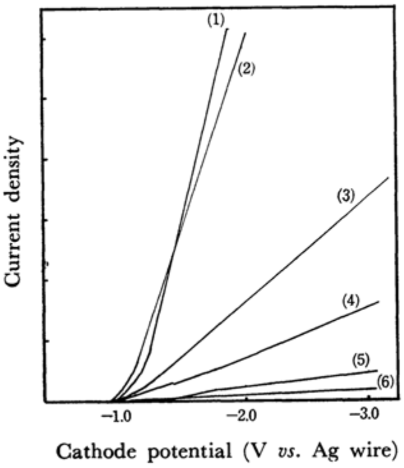

Fig. 2. Current-voltage relation.
(1) H_2O, (2) Methanol, (3) Methanol+HMPA (vol. ratio 1 : 1), (4) Ethanol, (5) 1-Propanol, (6) 2-Propanol; containing 0.5 M lithium chloride in all cases.

In these systems the addition of naphthalene (0.5 M) has little effect on the current-voltage curve. The decomposition voltages are nearly the same, about −1.0 V *vs.* Ag wire, in all these systems. In the methanol system, the current density is very high compared to that in the other alcohol systems. The current density at the same electrode potential decreases in the order: $H_2O\sim$methanol$>$ethanol$>$1-propanol$>$2-propanol, an order which agrees with the order of the decreasing dielectric constant or acidity. In the methanol system, the addition of HMPA depresses the current density by about half compared to the case of its absence; on the contrary, the addition of HMPA has little effect on the current density in the other alcohol systems.

Discussion

As has been described in the preceding section, the reduction of naphthalene does not take place in the absence of HMPA if the cathode potential is not extremely high, while naphthalene is effectively reduced even at cathode potentials lower than the polarographic half-wave potential if HMPA is added. These results suggest that the reduction of naphthalene is not caused through a direct electron-transfer mechanism in the present systems. The reduction mechanism is characteristic of an alcohol-HMPA system containing lithium chloride, as has been suggested by Sternberg *et al.*[6] They observed a dark blue color at the cathode during the electrolysis of lithium chroride in an HMPA-ethanol system, and suggested the generation of solvated electrons. These observations were confirmed in the present investigation, as will be described below.

When the electrolysis of lithium chloride in a pure HMPA system was carried out in an open H-cell with a diaphragm, the generation of dark blue globules was observed at the cathode after the evolution of gases. The globules disappear during the diffusion into the bulk solution and the liquid surface. When the electrolysis was carried out in a vacuum system, dark blue globules generate at the cathode, diffuse into the bulk, and disperse thoroughly in the cathode compartment. The coloration remains for several hours after the electrolysis.

When the vacuum electrolysis is carried out in the HMPA-ethanol system (volume ratio 1 : 1), a dark blue color is observed at the cathode surface, but it disappears during diffusion into the bulk. When naphthalene is added to this system, only a faint color is observed.

This coloration is the same as that observed in the system where alkali metals are dissolved in HMPA and shows a strong absorption band around 650 mμ. This absorption band is the same as that ascribed to the solvated electrons.[9] Moreover, it may be pointed out that the decomposition potentials in various HMPA-alcohol systems

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[9] M. Ottolenghi, K. Bar-Eli, H. Linschitz and T. R. Tuttle, *J. Chem. Phys.*, **40**, 3729 (1964).

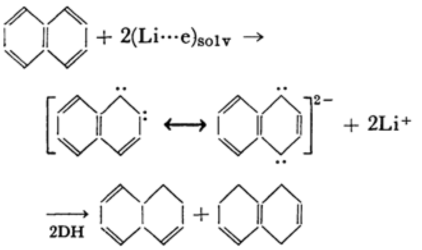
are nearly all the same, around -1.0 V *vs.* Ag wire. At the electrode potentials over this value, naphthalene is reduced effectively. This value is lower than that ascribed to the reduction of naphthalene.

These results show that the reduction of naphthalene proceeds according to a mechanism similar to that proposed by Krapcho *et al.*10) for the reduction of aromatic hydrocarbons by alkali metals in liquid ammonia and by Sternberg *et al.*4) for the electrolytic reduction of the benzene ring in ethylenediamine saturated with lithium chloride. The general reaction scheme is as follows:

$$\mathrm{Li^+} + \mathrm{e} \rightarrow (\mathrm{Li}\cdots\mathrm{e})_{\mathrm{solv}}$$
$$(\mathrm{Li}\cdots\mathrm{e})_{\mathrm{solv}} + \mathrm{R} \rightarrow \mathrm{Li^+} + \mathrm{R}^{\overline{\cdot}}$$
$$\begin{cases} \mathrm{R}^{\overline{\cdot}} + \mathrm{DH} \rightarrow \mathrm{RH} + \mathrm{D}^{\overline{\cdot}} \\ \mathrm{R}^{\overline{\cdot}} + (\mathrm{Li}\cdots\mathrm{e})_{\mathrm{solv}} \rightarrow \mathrm{R}^{2-} + \mathrm{Li^+} \\ \quad \mathrm{R}^{2-} + 2\mathrm{DH} \rightarrow \mathrm{RH_2} + 2\mathrm{D^-} \end{cases}$$

where R is an unsaturated compound to be reduced, DH is a proton donor, and $(\mathrm{Li}\cdots\mathrm{e})_{\mathrm{solv}}$ is the solvated lithium and electron.

It is proposed that naphthalene is reduced into dihydronaphthalene according to the following scheme:



It may be supposed from the polarographic results of the one-step two-electron reduction that the two-electron transfer occurs successively from solvated lithium to naphthalene in the first step of reduction. In the present systems, alcohols probably act as proton donors.

The selectivity of the reaction is affected by various factors: the kind of alcohols, the alcohol content, and the reduction potentials. In the ethanol-HMPA system, the hydrogenation proceeds more intensively with an increase in the ethanol content, as is shown in Fig. 1. This is reasonable when ethanol is considered to act as a proton donor. Dihydronaphthalenes are the main product when the HMPA content is high. In the methanol-HMPA and the 2-propanol-HMPA systems, the main products are dihydronaphthalene and tetralin; the yield of the former increases with an increase in the HMPA content.

It may be considered that the hydrogenation proceeds more extensively with an increasing acidity of alcohols and that, on the other hand, more strongly acidic alcohols react more intensively with solvated lithium and electrons, resulting in the hydrogen evolution. This is the reason why water does not act as a proton donor for the reduction of naphthalene and why extensively hydrogenated products are obtained only in a system consisting of ethanol, a moderately strong proton donor.

The increase in reduction potentials extensively encourages the hydrogenation as shown in Table 4 in the methanol-HMPA system. This result can also be understood in view of the fact that the solvated electrons increase in quantity with an increase in the potential.

In the 1-propanol-HMPA system, the main product is decalin. This result can not be interpreted from the standpoint described above; it is now being investigated further.

A detailed discussion of the selectivity of this reaction system will be reported in the near future, together with the results of the polarographic examination and of the reduction of benzene in similar systems.

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10) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).