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by

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Electrolytic Reduction of 1,4-; 1,5- and 1,8- Dinitronaphthalenes

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ABSTRACT

The polarographic reductions of 1, 4–;1,5–; and 1,8–dinitronaphthalenes were studied in two different solvent (N,N-dimethylformamide and pyridine) and four different supporting electrolyte.

Large-scale electrolytic reductions of these compounds in dimethyformamid were also studied. 1,5–diaminonaphthalene and 1–nitro, 4–amino naphthalene were isolated as a major reduçtion products of 1,5– and 1,4–dinitronaphalenes respectively. 1.8–dinitronaphalene gave resinous material mainly. During these studies graphite paste electrode was also used as a cathode and the controlled potential elecrolysis of these three dinitronaphthalenes were conducted under the new conditions.

INTRODUCTION

The polarographic behavior of the numerous dinitroderivatives of benzene has been investigated by Pearson [1,2] Holleck and others, but wery little work has been done with the nitronaphthalene series. [3,4,5]

In this work the polarographic studies and large-scale reduction of three dinitronaphthalene were done in different solvents, various supporting electrolytes, cathodes and cells.

EXPERIMENTAL

Chemicals: N,N–dimethylformamide puriss grade and purified according to Wawzonek [6]. Pyridine was puriss grade and was used without further purification. Tetra-n-butylammonium tetrafluorobarate was prepared from tetra-n-butylammonium bromide and HBF_4 according to House [7] The other tetraalkylammonium salts were puriss grade and obtained from Fluka. 1,5–and 1,8–dinitronaphthalrnes were obtained from Fluka and 1.4–dinitronaphthalene was prepared by previously published procedure and purified by chromatography on the alumina column. Chloroform was used as an eluent for this. [8]

Apparatus and general procedure: The polarographic curves were recorded using a Shimadzu Polarograph RP 50. Current potential curves for the graphite paste electrode were obtained by using Wenkings potentiostat and stepping motor. For the study of the polarographic behaviour a Kalousek vessel with a separated saturated calomel electrode (S.C.E.) was used. The cappillary used had a drop-time of $t_1 = 4{,}1$ s and out-flow velocity of mercury 6,3 mg/s.

For the identification of products. Perkin Elmer 377 IR and Beckmann DB-G UV spectrometers were used. Molecular weights were determined by Perkin Elmer Hittachi molecular weight apparatus.

Controlled potential electrolysis-In this work two different type of electrolytic cell were used. One of them has been used during the reduction of dinitronaphthalenes at mercury cathode and in a nonaqueus media. This cell consisted in a three necked 500 ml beaker. One neck was fitted with a nitrogen inlet and second with a nitrogen outlet. The center neck was fitted with a anode

compartment and the reference electrode was separeted from the working electrode by Luggin capillary and tap; the working and auxillary electrodes were separeted by glass frits. The auxillary electrode was a graphite rod. All potentials in this paper are quoted versus S.C.E. The working electrode was a triply distilled mercury of area 314 cm^2. The volume of catholyte and anolyte were 100 ml and 20 ml respectively.

Tetra-n-butylammonium salts were used as a supporting electrolyte. Dissolved oxygen was removed from the catholyte and anolyte by bublling prepurified nitrogen through the solution for 20 minutes. Preelectrolysis of the catholyte without depolarizer was carried out at the corresponding potential value until the current was dropped to a negligible value, then the circuit was opened and 1 g powdered dinitronaphthalene was introduced and nitrogen was bubled through the cell for 30 minutes. At the end of this period, the circuit was closed again and the electrolysis was started. The nitrogen bubling was continued until the run was finished. The electrolysis was allowed to continue until the current dropped to the minimal value. At the end of the electrolysis catholyte was poured into the distilled water, precipitation was occured, the precipitate was filtered and extracted with ethanol. The ethanol extract was then evaporated to dryness and the products were chromatographed on alumina (Merck grade 1). The eluent at the start was petroleum ether which was gradualy changed to chloroform, then to ethanol until all fractions had come down. Usually only one major product was obtained and identified by means of IR, UV, NMR spectrorometers and comparision with an authentic samples and/or literature data [13,14] The other fractions consisting of tarry polymeric material and byproducts. The IR spectra of these compounds showed aliphatic carbonhydrogen bands around 3.40 μ and nitrogen-hydrogen bands around 64 u [10].

The second cell which was used in this work during the reduction of dinitronaphthalenes at graphite paste electrode and in an aqueus media. It was consisted in a 50 ml beaker. Soxhlet extraction paper thimble was used as a diafram and in the same time as a cathode compartment. 20 gr powdered graphite was mixed with a 1 g depolarizer and 10 ml 0,1 N sodyumhydroxide solution in water. This graphite paste was placed into the thimbles and used as a cathode. Graphite rod was introduced into this paste for making contact with negative pole of the potentionstat. Three or four graphite rod were connected each other in a series and was placed around of the soxhlet thimbles and used as an anod. Reference electrode (SCE) was introduced into the cathode paste. The beaker was filled with 0,1 N sodiumhydroxide solution. The circuit was closed again and the electrolysis were carried out at the corresponding potential value.

At the end of the electrolysis the soxhlet thimbles was placed into the soxhlet extraction apparatus and extracted with ethanol. The ethanol extract was then evaporated to dryness and the products were chromatographed on alumina (Merck grade 1). Petroleum ether, chloroform and ethanol were used an eluent succecively. The same major products were obtained in this experiment too, but the quantity of the resinous material and byproducts was decreased and their IR spectra showed no carbonhydrogen aliphatic bonds near 3.40 μ.

All the controlled potenital electrolysis were carried out at 25°C cell temperature and at the first polarographic half-wave potentials.

RESULTS AND DISCUSSION

In this work the effect of solvent on the polarographic halfwave potentials and also on the reduction results of electrosynthesis were studied. Pyridine and N,N-dimethyformamide were used as a solvent for both experiments and it was observed that the polarographic reduction of these compounds in pyridine were easear then in DMF, but the polarograms which were obtained in DMF were well defined as compared to polarograms in pyridine.

In the Table I the controlled potential electrolysis of 1,8–dinitronaphthalene in two different solvent are given.

TABLE I

Controlled potential electrolysis of 1, 8–dinitronaphtale in two different solvent

SOLVENT	Supporting electrolyte duration		Reaction products
DMF	TBABr	3,5 h	Resin and at least 7 different by-products.
pyridine	TBABr	5 h	100 % resin

Although we were not be able to identiy any specific reduction products in both solvents, 100 % resinous material was isolated as a reduction product of dinitronaphthalene in pyridine, at least seven different by-products with the resinous material were obtained during the reduction of dinitronaphthalene in DME. This shows that changing solvents were effected the reaction pathways and products, therefore DMF was used throughout experiments.

The half-wave potentials of three dinitronaphthalenes in DMF and four different supporting electrolytes are given in table II. The ease of reduction increases in the order of $TBABF_4 <$ TEAI <TBAI <TBABr.

TABLE III

Polarographic reduction of three dinitronaphtalenes in DMF.

Supporting	1,8–dinitronapthale		1,5–dinitronapthale		1,4–dinitronapthale	
electrolyte	$E_{1/2}$*	$i_{1/d}$	$E_{1/2}$	$i_{1/d}C$	$E_{1/2}$	$i_{1/d}C$
TEAI	-0.910	3.3	-0.820	3.3	-0.565	3.4
	-1.560	8.4	-0.970	5.9	-0.765	6.4
	-1.850	15.4	-1.820	9.4		
			-2.010	15.6		
TBAI	-0.896	3.4	-0.777	3.7	-0.540	3.4
	-1.546	9	-0.987	5.7	-0.740	6.4
	-0.897	3.4	-0.746	3.8	-0.490	3.4
TBABr	-1.582	9	-0.956	6.8	-.680	6
	-0.932	3.4	-0.787	3.6	-0.555	3.4
$TBABF_4$	?	?	-1.007	6.4	-0.775	6.3

*The values of $E_1/_2$ are in volts ve SCE and those of id/C are in μa/mmole/l. A question mark indicates that the wave is too indefinite to assign values with any degree of certainity.

The polarographic reductions of the ten different dinitronaphthalene were studied by Boyd [9] and according to his results, reductions proceeds in a stepwise manner and the first polarographic step was corresponds to a four electron transfer. This has been interprated as the reduction of one of the nitro groups to a hydroxylamino groups. However his experimental results showed that 1.8–dinitronaphthalene was the only compound that did not exhibit this characteristic behaviour. Instead it gave an initial wave that corresponded to either eight or ten electron transfer depending on the acidity of the solution. It was suggested that this might be due to the formation of the ring compound 1,8–naphtopyrazole. But our results showed that controlled potential electrolysis of 1,8–dinitronaphthalene yielded very high melting highly coloured, nitrogen contained materials which appear to be polymeric.

On the other hand, among the reduction products of 1.5– and 1.4–dinitronaphthalenes formation of hydroxylamino compound were not observed. But 1.5–naphthalendiamine and 1–amino– 4–nitronaphthalene were obtained as a major products and too much by-products and resinous material were isolated from the reduction reactions of these compounds.

The infrared spectra of some these tarry residues and by-products showed aliphatic carbon-hydrogen bands around 3.40 μ [10]. This shows that the presence of the tetraalkylsalts (which were used as a supporting electrolyte) and DME (which was used as a solvent) in reaction media, interfere with the cathode reactions and causes so many chemical side reactions.

The reduction of aromatic compounds, proceeds via the anion radicals which have been shown directly by E.S.R. studies. [11] This is also explane the existance of so many by-products and the resinous material. [12]

S. Wawzonek showed in his studies that mercury cathode also interfere with the cathode reactions [6].

Owing to the difficulties mentioned above, we decided to make some necassary alterations in the system. Thus, we used graphite paste instead of mercury, and 0.1 N NaOH in water as an electrolyte. Cell number II has been used in these experiments and current-potential curves for the new reaction conditions has been obtained and The values of the reduction potentials has been taken from this graph and electrolysis were carried out at these potentials. The results of the electrochemical reductions of dinitronaphthalenes on graphite paste electode are shown in Table III.

1,8–dinitronaphthalen gave resinous material in this experiment too. On the other hand 1,5–naphthalenediamine and 1–

TABLE III

Controlled potential electrolysis of three dinitronaphthalene at graphite paste electrode

Compound	Reduction potential	Reaction products
1,8–Dinitronaphthalene	-0.850 V(SCE)	Resinous material and 1.8–dinitro naphthalene (1)
1,5–Dinitronaphthalene	-0.870 V(SCE)	35 % 1.5–diaminonaphthalene (2) resim, 1.5–dinitronaphthalene, and very little by-products.
1,4–Dinitronaphthalene	-0.600 V(SCE)	5 % 1–nitro, 4–amino naphthalene (3) and at least 20 different by-products (4).
1,4–Dinitronaphthalene	-0.850 V(SCE)	25 % 1–nitro, 4–amino naphthalene and 3 different by-products (5).

1. Rather great amounts of starting materials recovered due to the very weak solubility of these compounds in electrolyte which were used during the electrolysis.
2. This compound was isolated from the ethanol extract of graphite paste (fig 1)
3. Fig 2 and 3.
4. These by-products were observed on the thin-layer plate.
5. All percentages were given by weight.

amino 4–nitro naphthalene has been obtained as a reduction products of 1,5–and 1,4–dinitronaphthalenes respectively.

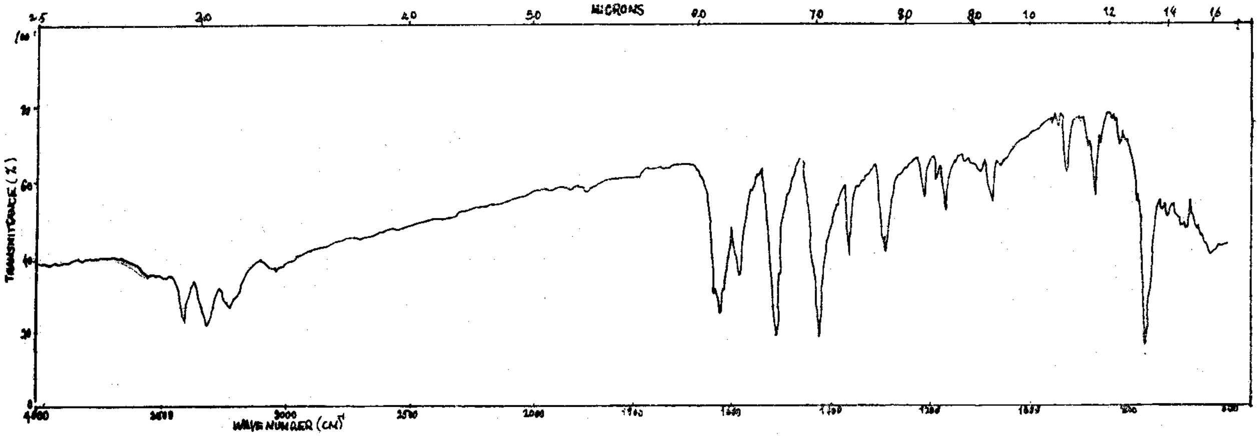
The effect of the new reduction conditions has been observed on the quantity of the by products. Only a few by-products were observed and IR spectra of all these by-products showed no carbon-hydrogen aliphatic bonds near 3.40 μ. This can be explaned that:

Reduction of this compounds in DMF/TBAX, the protons are obtained by the following process:

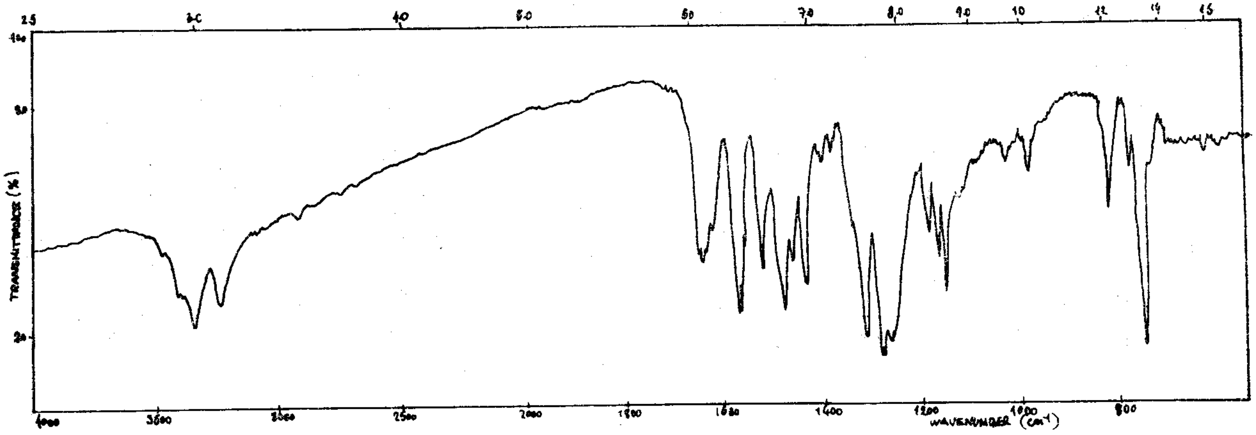
$$B^- + CH_3CH_2CH_2CH_2N^+Bu_3 \longrightarrow BH + CH_2{=}CHCH_2CH_3 + NBu_3$$

The alkene may react further. Therefore we do not get "aliphatic" impurties in aqueous solution where we just get a higher concentration of OH^-.

The poor contact between the electrolyte and the cathode cake due to improper wetting and bad contact between the conducting electrolyte and nonconducting organic compound are



The IR spectrum of 1.5–Naphthalenediamine (KBr disk)



The IR spectrum of 1–Amino, 4–nitro naphthalene (KBr disk) the main disadvantages of the second cell, but the decrease in the amount of the side reactions, ease of the cell preparation and usage are the main advantages of the second cell.

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ÖZET

Bu çalışmada 1,4–;1,5– ve 1,8–dinitronaftalinlerin polarografik indirgenmesi iki farklı çözücü içinde (dimetilformamid ve pridin) ve 4 farklı destek elektroliti içinde yapıldı.

Kontrollu potansiyelde preparatif elektroliz 1. Cıva katodda 2. Grafik katodda olmak üzere 2 farklı elektrodda yapıldı ve indirgenme ürünleri olarak 1.4–dinitronaftalin için 1–nitro, 4–amino naftalin; 1,5–dinitronaftalin için a.5–naftalin diamin ve 1,8–dinitronaftalin içinde reçine elde edildi.

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