COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 22 B ANNÉE 1975

Electrochemical Preparation of Dinitroazoxybenzenes

by

CELÂL TÜZÜN and TARIK PEKEL

1

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

---

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifique représentées à la Faculté.

La Revue, Jusqu'a 1975 à l'exception des tomes I, II, III, etait composé de trois séries

Série A : Mathématique, Physique et Astronomie.
Série B : Chimie.
Série C : Sciences naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A_1: Mathématique
Série A_2: Physique
Série A_3: Astronomie
Série B : Chimie
Série C_1: Géologie
Série C_2: Botanique
Série C_3 Zoologie

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Adresse: Fen Fakültesi Tebliğler Dergisi, Fen Fakültesi, Ankara, Turquie.

Electrochemical Preparation of Dinitroazoxybenzenes*

CELÂL TÜZÜN and TARIK PEKEL**

(Department of General Chemistry, Faculty of Science, University of Ankara)
Ankara, Turkey

(Received March 3, 1975)

ABSTRACT

The elctrolytic reduction of dinitrobenzenes under the controlled potential at pH 11 has been studied. Azoxy compounds have been found as the main reduction products of these compounds.

INTRODUCTION

The electrolytic reduction of aromatic nitro compounds have been investigated using a number of different electrodes and variety of experimental conditions. The formation of products was found to be dependable on the electrode materials, electrolyte solutions and pH values. [1–3]

Generally the reduction of nitro compounds in acid solutions yields amino derivatives on occation hydroxylamino and benzidine were formed depending to the cathode material. The electrochemical reduction of nitro compounds in alkaline media shows difficulties, because of secondary chemical reactions. Although electrochemical reductions of dinitrobenzenes in acid and neutral media have been extensively investigated over a 50 years, but very little work has been done for these compounds in alkaline media.

---

* This paper is a part of a thesis submittted to the Faculty of Science, University of Ankara in partial fulfillment of the requirements for the degree of Doctorate (Ph. D) by Tarık Pekel.

** Mailing adress: Ankara Üniversitesi, Fen Fakültesi, Genel Kimya Kürsüsü Ankara, Turkey.

The polarographic behavior of dinitrobenzenes have been investigated by Pearson [4], Holleck and Schmidt [5–6]. Macroscale electrochemical reductions of these compounds under the constant current have been carried out by King [7].

In this work preparative reduction of three dinitro substituted benzene on mercury pool electrode in an aqueous solution have been investigated. Dinitroazoxybenzenes have been isolated as a major reduction product.

EXPERIMENTAL

Dinitrobenzenes were chromatographed on aluminyum oxide grade l (Merck) and recrystalized before using. Borax standart buffer solution pH 11 was used as a buffer solution. The cell was thermostated at 0°C±0,5;25°C±0,5 and 50°C±0,5.

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

Electrolysis were carried out at a stirredmercury cathode at pH 11. Potentials were maintained constant by fully transistorized potentiostat at the values which were taken from the polarographic curves. [5–6]

The electrolytic cell consisted in a 4-necked 500 ml beaker. One neck was fitted with a nitrogen inlet and the second with a nitrogen outlet. The center neck was fitted with 50 ml porous cup which served as the anode compartment. The anode was a graphite rod in contact with 40 % K_2CO_3 solution as the anolyte. Triply distilled mercury was used as cathode. The remaining neck was fitted with a saturated potasyum chloride reference electrode, stirring was performed by magnetic stirrer using a teflon covered stirring bar. Dissolved oxygen was removed from the catholyte by bubling nitrogen through the solution 20 minutes. Preelectrolysis of the catholyte, consisting of 100 ml buffer solution was carried out at the corresponding potential values until the current droped to a negligible value, then the circuit was opened and 1 gr powdered dinitrobenzene 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. During the electrolysis, nitrogen flows was also continued.

The electrolysis was allowed to continue until the current dropped to the minimal value.

At the end of the electrolysis catholyte was filtered and the residue was extracted twice with benzene and the combined extract was chromatographed on aluminyum oxide grade 1. Chloroform was used as eluent. Purified product was identified by means of IR, UV, NMR, Mass and comparison with authentic samples and/or literature date [8–9] (Fig 1,2,3)

Because of two different platos have been observed on the polarographic curves the electrolysis of each dinitrobenzenes were carried out at two different potential values. And each run was also carried out at three different temperature due to observing the effect of temperature to the reaction products and their yields.

RESULTS AND DISCUSSION

It can be seen from the table I that as the cell temperature increases the amount of the azoxy compounds and the resin increases. It is because of increasing solubility of dinitrobenzenes. It is found that reduction of o-dinitrobenzene is more difficult then the m- and p- isomers. This is in good agreement with the findings of Pearson who found that it is more difficult to reduce o-nitrotoluene than either m-or p-nitrotoluenes. Holleck has been reported that reduction of o- and p- dinitrobenzenes in alkaline solutions at the potential of the first polarographic wave mainly yields o- and p-nitrophenylhydroxylamine respectively. However our experimental results showed that in the absence of maximum supressor the main reduction products of dinitrobenzenes at the potential of the first polarographic wave are the corresponding dinitroazoxybenzenes. The main factor in the change of the reduction products in this work is the change of experimental conditions of the reduction. In our work the duration of the reducti-

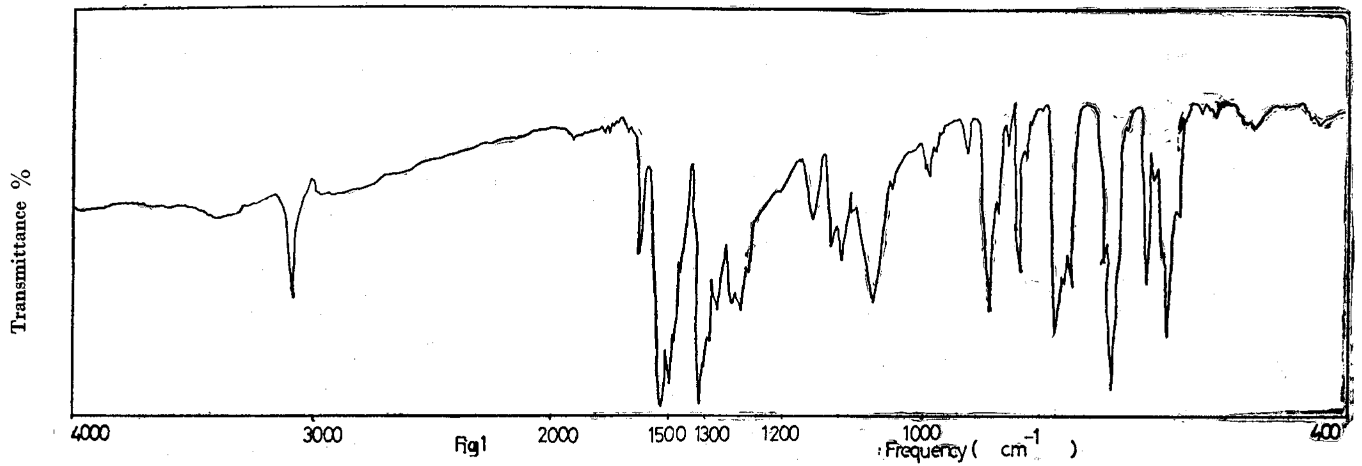


Fig1

IR spectrum of 3,3'-dinitroazoxybenzene (KBr disc)

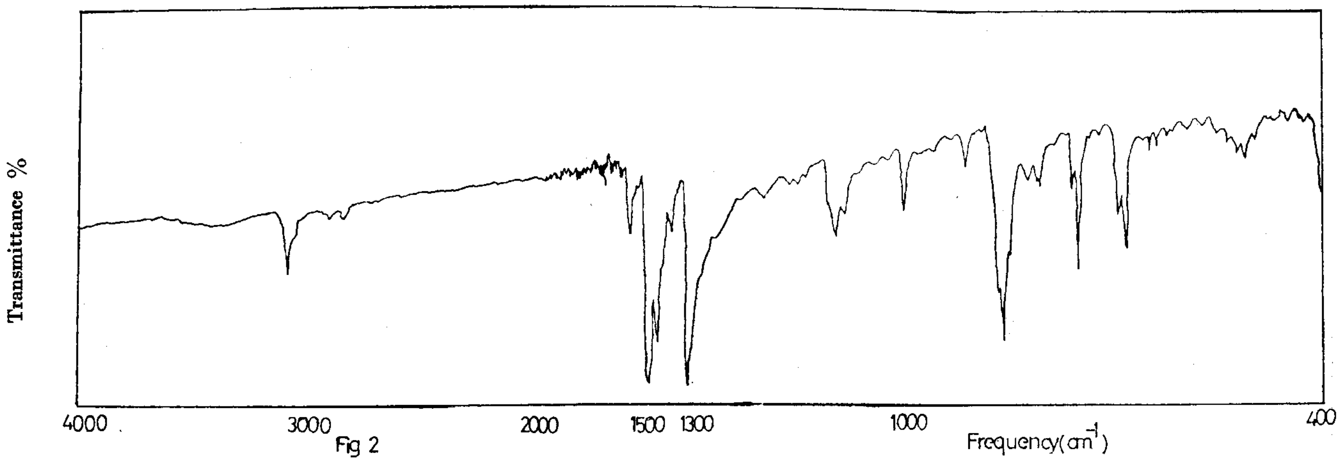


Fig 2

IR spectrum of 4,4'-dinitroazoxybenzene (KBr disc)

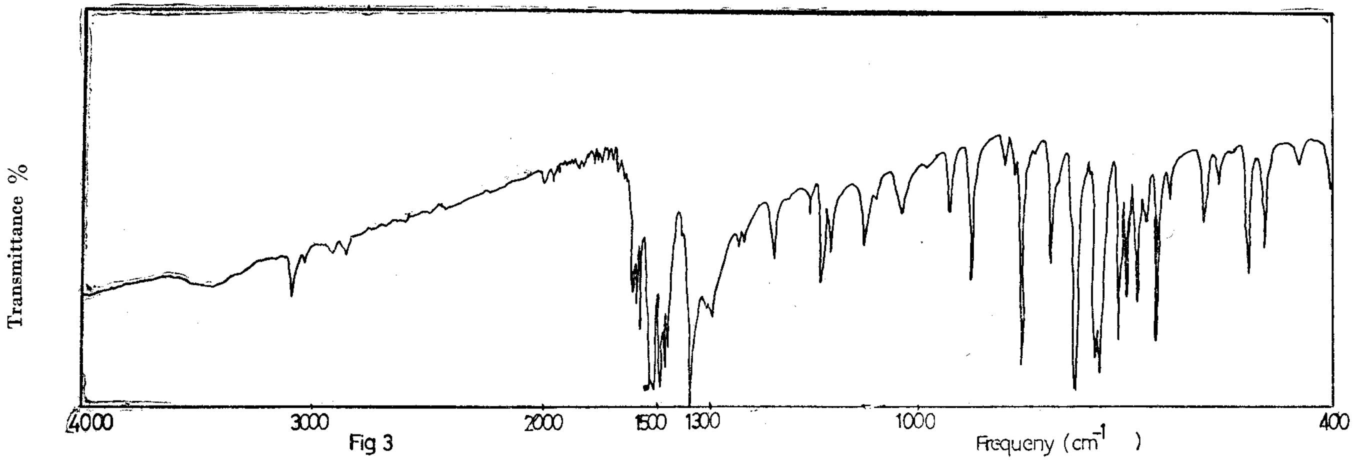


Fig 3

IR spectrum of 2,2'-dinitroazoxybenzene (KBr disc)

TABLE 1.

Reduction Product of Dinitrobenzenes at mercury cathode

Compound	Electrode potential	cell temperature	main product (% yield)*	secondary product (% yield)	tarry residue (% yield)
m–dinitrobenzene	–0,600 V	0°C	m-dinitrobenzene(60)	3,3'dnitroazoxybenzene(35)	(5)
m–dinitrobenzene	–0.600 V	25°C	3,3'dinitroazoxybenzene(60)	m–dinitrobenzene(28)	(12)
m–dinitrobenzene	–0,600 V	50°C	3,3'dinitroazoxybenzene(78)	m–dinitrobenzene(4)	(18)
m–dinitrobenzene	–1,040 V	0°C	——	——	(100)
m–dinitrobenzene	–1,040 V	25°C	——	——	(100)
m–dinitrobenzene	–1,040 V	50°C	——	——	(100)
p-dinitrobenzene	–0,400 V	0°C	4,4'dinitroazoxybenzene(50)	p-dinitrobenzene(45)	(5)
p-dinitrobenzene	–0,400 V	25°C	4,4'dinitroazoxybenzene(70)	p-dinitrobenzene(20)	(10)
p-dinitrobenzene	–0,400 V	50°C	4,4'dinitroazoxybenzene(82)	p-dinitrobenzene(6)	(12)
p-dinitrobenzene	–1,200 V	0°C	——	——	(100)
p-dinitrobenzene	–1,200 V	25°C	——	——	(100)
p-dinitrobenzene	–1,200 V	50°C	——	——	(100)
o-dinitrobenzene	–0,700 V	0°C	o-dinitrobenzene(83)	2,2'dinitroazoxybenzene(12)	(5)
o-dinitrobenzene	–0,700 V	25°C	o-dinitrobenzene(70)	2,2'dinitroazoxybenzene(14)	(8)**
o-dinitrobenzene	–0,700 V	50°C	o-dinitrobenzene(57)	2,2'dinitroazoxybenzene(18)	(15)***
o-dinitrobenzene	–1,200 V	0°C	o-dinitrobenzene(30)	——	(70)
o-dinitrobenzene	–1,200 V	25°C	o-dinitrobenzene(25)	——	(75)
o-dinitrobenzene	–1,200 V	50°C	o-nitroaniline(15)	——	(85)

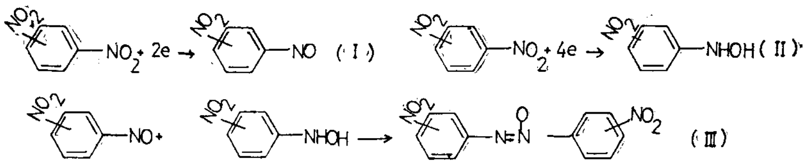
* By weight, the yields are calculated on the basis of the amount of starting material.

** 8 % o-nitroaniline has been obtained as a tertiary product

*** 10 % o-nitroaniline has been obtained as a tertiary product on was 8 to 30 hours and somecases was 77 hours. In the case of o-dinitrobenzene probably the steric hindrance between two nitro groups prevent the condensation step of the reaction and lovers the yield.

The reduction of dinitrobenzenes, like those of aromatic nitro compounds proceeds via the anion radical which has been shown directly by electron spin resonance studies. [10–13]

Simplified scheme of the formation of dinitroazoxybenzenes from the reduction of dinitrobenzenes are given below:



Probably nitro nitroso benzenes which formed in the first step of the reduction may act as an electrophill toward nitrophenylhydroxylamine with the formation of dinitroazoxybenzenes in the alkaline media, so that an electrochemical reactions follows a chemical condensations during the formation of azoxy compound.

Dark resin has been isolated as a reduction products of dinitrobenzenes at the potential of second polarographic waves. Those might be polimeric products of phenylenediamines. IR spectra of the resins show broad bands at the 3400 cm^{-1} and 1500 cm^{-1} due to the N-H and C-N bonds. [9]

The existance of large amounts of unreacted starting material (in Table I) can bee explaned such a way that some of the tarry materials, that was precipitated on the undissolved starting material prevent the dissolution of the discussed compounds.

Acknowledgement-This study was supported by the Scientific and Technical Research Council of Turkey. (Project No. TBAG-110).

REFERENCE

[1] C.J. Brockman, Electroorganic Chemistry, John Wiley and sons, N.Y., 1926.

[2] M.J. Allen, Organic Electrode Proceses, Reinhold Publishing Corp., N.Y. 1958.

[3] Manuel M. Baizer, Organic Electrochemistry, Marcel Dekker Inc. N.Y. 1973.

[4] J. Pearson, Trans. Faraday Soc. 44 (1948) 683.

[5] L. Holleck und H. Schmidt, Z. Electrochem. Ber. Bungenges. physik. Chem. 59, 56 (1955).

[6] L. Holleck und H. Schmidt, Z. Electrochem. Ber. Bunsenges. physik. Chem. 59, 1039 (1955).

[7] M.V. King, J. Org. Chem., 26, 3323 (1961).

[8] P.H. Gore and O.H. Wheeler, J. Am. Chem. Soc. 78, 2162, 1956.

[9] L.J. Bellamy, "The Infrared Spectra of Complex Molecules" Wiley, 1966.

[10] Freed, Fraenkel, J. Chem. Phys. 41 (1964) 699.

[11] Faber, Fraenkel, J. Chem. Phys. 47 (1967) 2462.

[12] Allendoerfer, Rieger, J. Chem. Phys. 56 (1967) 3410.

[13] Gutch, Waters, Symons, J. Chem. Soc. B. (1970) 1261.

ÖZET

Bu çalışmada dinitrobenzenlerin preparatif elektrolizi kontrollu potansiyelde ve geniş yüzeyli cıva katodda yapılmıştır. Elektroliz için zorunlu indirgenme potansiyelleri L. Holleck [5–6] tarafından yapılmış olan çalışmadan alınmıştır. İndirgenme ürünleri önce kromatografik yöntemlerle saflaştırılmış ve daha sonra IR, UV, NMR ve kütle spektrumlarından yararlanılarak teşhisleri yapılmıştır.

Dinitrobenzenler için indirgenme ürünü olarak başlıca dinitroazoksi bileşikleri elde edilmiştir. Reaksiyon sonuçlarından en yüksek verimle p– bileşiğinin indirgendiği ve bunu m– ve o– bileşiklerinin takip ettiği görülmüştür.

Prix de l'abonnement annuel

Turquie : 15 TL; Étranger: 30 TL.

Prix de ce numéro : 5 TL (pour la vente en Turquie).

Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı Ankara, Turquie.

Ankara Üniversitesi Basımevi. Ankara – 1975