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Electrochemical Preparation of Dinitroazoxybenzenes

by

CELĂL TÜZÜN and TARIK PEKEL

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie
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Electrochemical Preparation of Dinitroazoxybenzenes*

CELÂL TÜZÜN and TARIK PEKEL**

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

Ankara, Turkey

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ABSTRACT

The electrolytic 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 octation 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 submitted to the Faculty of Science, University of Ankara in partial fulfillment of the requirements for the degree of Doctorate (Ph. D) by Tarik Pekel.

** Mailing address: Ankara Universitesi, 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 I (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 stirred mercury 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 % K₂CO₃ solution as the anolyte. Tripily 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 bubbling nitrogen through the solution 20 minutes. Pre-electrolysis of the catholyte, consisting of 100 ml buffer solution was carried out at the corresponding potential values until the current dropped 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 aluninyum 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 data [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 suppressor the main reduction products of dinitrobenzenes at the potential of the first polarographic wave are the corresponding dinitroazoxoxybenzenes. 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-
IR spectrum of 3,3'-dinitroazoxybenzene (KBr disc)
IR spectrum of 4,4'-dinitroazoxybenzene (KBr disc)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Electrode potential</th>
<th>cell temperature</th>
<th>main product (% yield)</th>
<th>secondary product (% yield)</th>
<th>tarry residue (% yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-dinitrobenzene</td>
<td>-0.60 V</td>
<td>0°C</td>
<td>m-dinitrobenzene (90)</td>
<td>3,3'-dinitroazoxybenzene (45)</td>
<td>3,3'-dinitroazoxybenzene (70)</td>
</tr>
<tr>
<td>m-dinitrobenzene</td>
<td>-0.60 V</td>
<td>25°C</td>
<td>m-dinitrobenzene (90)</td>
<td>3,3'-dinitroazoxybenzene (45)</td>
<td>3,3'-dinitroazoxybenzene (70)</td>
</tr>
<tr>
<td>o-dinitrobenzene</td>
<td>-0.60 V</td>
<td>50°C</td>
<td>o-dinitrobenzene (90)</td>
<td>3,3'-dinitroazoxybenzene (45)</td>
<td>3,3'-dinitroazoxybenzene (70)</td>
</tr>
</tbody>
</table>

* By weight, the yields are calculated on the basis of the amount of starting material.
** 8 % o-anilinomine has been obtained as a tertiary product.
*** 10 % o-anilinomine has been obtained as a tertiary product.
on was 8 to 30 hours and some cases 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 lowers 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:

\[
\begin{align*}
\text{NO}_2^- + 2e^- & \rightarrow \text{H}_2\text{O} \tag{I} \\
\text{NO}_2^- + 4e^- & \rightarrow \text{H}_2\text{O} + \text{HNOH} \tag{II} \\
\end{align*}
\]

Probably nitro nitroso benzenes which formed in the first step of the reduction may act as an electrophil 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 explained such a way that some of the tarry materials, that was precipitated on the undissolved starting material prevent the dissolution of the discussed compounds.

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ÖZET


Dinitrobenzener için indirgeme ürünü olarak başlıca dinitrozaksi bileşikleri elde edilmiştir. Reaksiyon sonuçlarından en yüksek verimle p- bileşiğinin indirgendiği ve bunu m- ve o- bileşiklerinin takip ettiği görülmüştür.
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