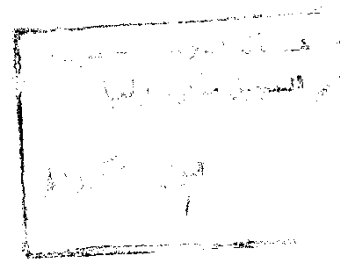
STUDIES OF SOME OXIDATION AND REDUCTION REACTIONS BY ELECTROCHEMICAL METHODS

THESIS SUBMITTED



BY

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Studies of Some Oxidation and Reduction Reactions by Electrochemical Methods.

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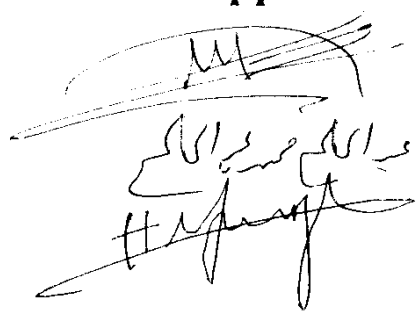

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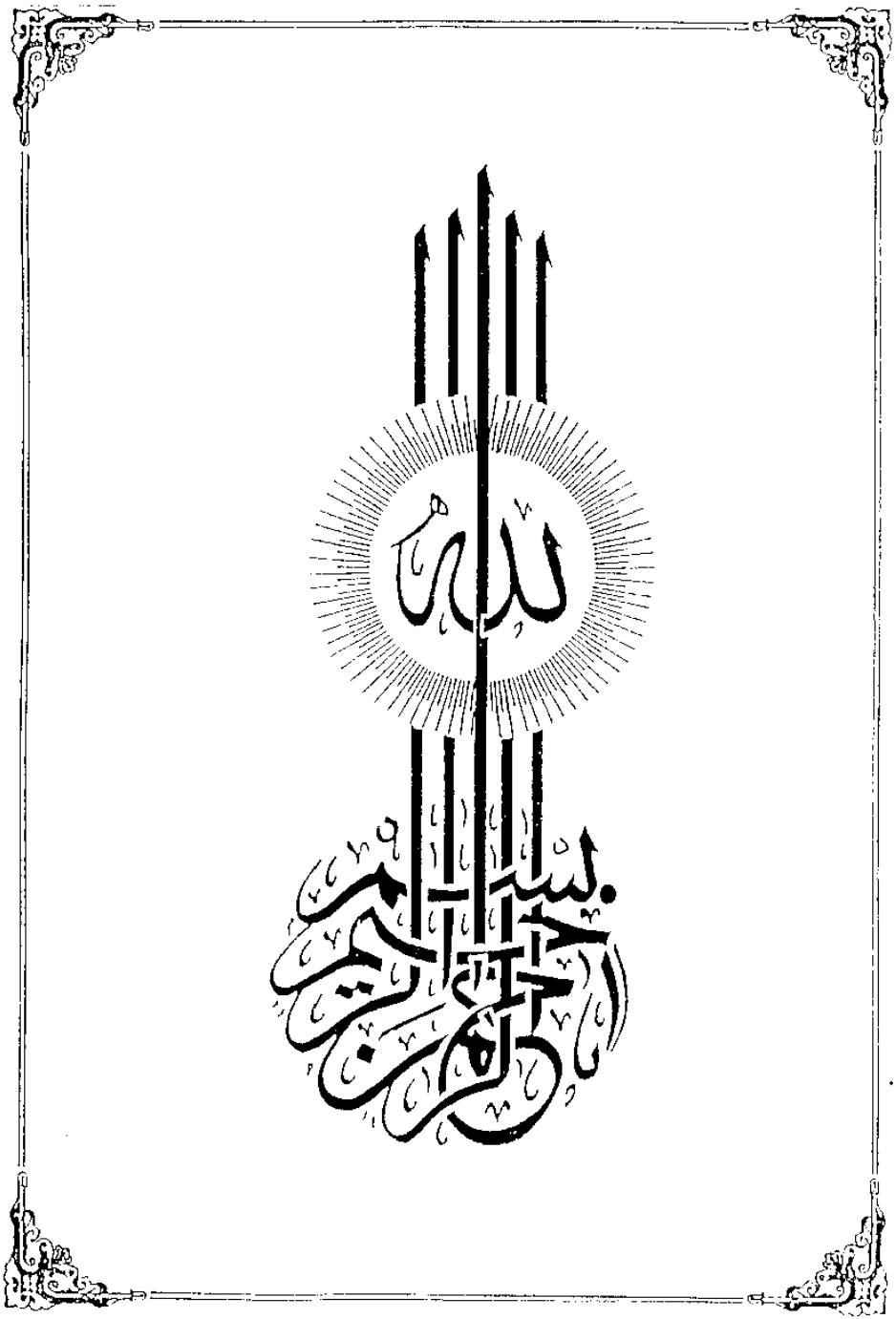

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To My Wife

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CONTENTS

AIM AND STRUCTURE OF THE WORK

1.Aim and structure of the work

Electrochemical methods can often be applied to understand chemical reactions. In this work a detailed electrochemical study of substituted benzenesulfonamide was carried out in order to obtain information on the application of these compounds in certain technical processes e.g. in photographic chemistry.

All compounds were studied intensively by means of cyclic voltammetry and rotating disc electrode measurements. Both the application of these methods and the results obtained by varying several parameters like concentration, pH, scan rate, rotation speed of the electrode, etc. will be discussed with one compound in detail. The results obtained for the other four compounds will then be presented in a comparative way. By this procedure, several handreds results could be summarized in a relatively short manner.

The aim of this work was to give a short but thorough introduction into the opportunities which certain electrochemical methods will offer, in the field of electrochemistry.

Thus we aimed to get :

a) A short but thorough introduction into fundamental electrochemical procedures based on disc electrodes.

b) A demonstration of the application of electrochemical methods for the analysis of both homogeneous and heterogeneous redox reactions

c) A thorough study of some benzenesulfonamide which may allow their use in photographic processes.

INTRODUCTION

2. INTRODUCTION

2.1. Organic electrode reactions

Electro-organic reactions are organic reactions taking place at the surface of the electrode.There are two types of electro-organic reactions:
(a) The direct or heterogeneous type and
(b) The indirect or homogeneous type.

(a). Heterogeneous organic electrode reactions

A heterogeneous, or direct, electro-organic reaction is one in which the organic compound exchanges electrons directly with the electrode. The fundamental event in such reactions is the electron transfer at the electrode-solution interface.

This reaction involves three basic steps :

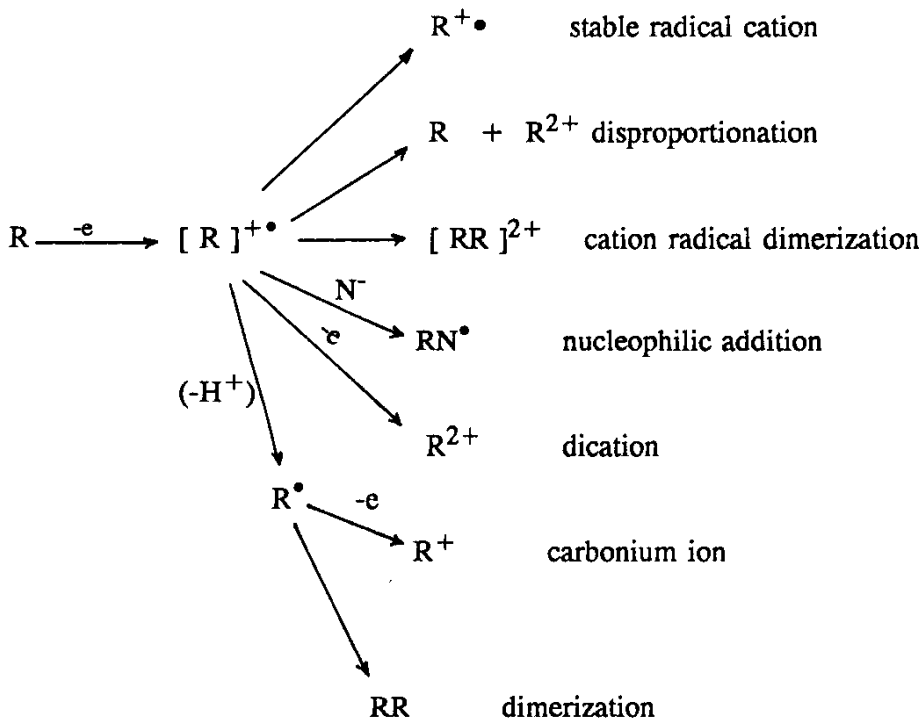
1. Transfer of electroactive substance from the bulk of the solution to the electrode surface or the region of the electrical double layer.
2. Exchange of electrons between electrode and electro-active species. Adsorption may be involved here.
3. Removal of the primary electrode products from the electrode surface. Desorption may be involved here.

The slowest of these steps determines the overall reaction rate.

Scheme 1 represents the direct oxidation reaction at the electrode surface.

(b). Homogeneous organic electrode reactions

A homogeneous, or indirect, electro-organic reaction is one in which the organic compound does not exchange electrons with the electrode directly but by the intermediation of an electro-active substance. Electron transfer and chemical reactions take place in the bulk of the solution until the stable products are obtained. Indirect reactions also can occur heterogeneously when one or more of the reactants or the electron mediators are adsorbed or immobilized at the electrode surface.



Scheme 1 direct oxidation reactions at electrode surface

2.2. Literature review

In the literature on electrochemistry, there is a lack of studies on the electrochemical oxidation of benzenesulfonamide derivatives. No attempts have been made to study the mechanism of electro-oxidation of these compounds in particular. The literature on benzenesulfonamide and its derivatives is almost entirely based on their reduction, usually at mercury electrodes[1-4].

The electrochemical reduction of benzenesulfonamide and its ortho, para, and meta derivatives was examined[2] in aprotic medium with varying experimental conditions, i.e. drop time, concentration and temperature. It was found that the reduction process is irreversible and controlled by diffusion at low concentrations and drop times, whilst the

whole process is controlled by adsorption at higher concentrations and drop times.

The polarographic study of a series of N-substituted benzenesulfonamide and their p-amino derivatives, in aprotic and protic media, has been investigated[3]. The electrochemical reduction of these compounds involves the S-N bond cleavage. It was also found that the effect of the substituents on the amidic nitrogen on the half-wave potential is independent of the protonicity of the solvent used, so the half-wave potential value can be regarded as a good structure index. From the polarographic data, a series of polar inductive substituent constants are obtained, the validity of which have been proved also by comparison with other experimental physicochemical parameters of these compounds in relation to their molecular structures.

The polarographic reduction in an aprotic solvent of a series of 19 sulfonamide derivatives has been studied[4]. The study includes the evidence of the C-S-N moiety as the electro-active center for the electron uptake, the preference of the S-N bond over the S-C bond for the reductive cleavage, and also a relationship between the half-wave potential and the energy of the Lowest Unoccupied Molecular Orbital (LUMO).

The electrochemical reduction of compounds having the $-SO_2NHOH$ group was studied, to determine whether the product would be a sulfonamide or a thioamine[5]. The polarographic characteristics of sulfur aromatic N-hydroxysulfonamides were studied using a dropping mercury electrode in 0.1M KCl as a supporting electrolyte. The hydroxysulfonamide compounds are reduced solely to their respective sulfonamides.

The reduction of benzenesulfonamides at a mercury cathode in acetonitrile / Et_4NBr solutions has been studied[6] using cyclic voltammetry, ESR spectroscopy and large scale electrolysis with chemical product identification. Their results agree in general with those of Horner et al.[7,8] in that they observe the cleavage of S-N bonds. They found that proton availability influences the course of the reaction of certain compounds. Cyclic voltammograms of p-toluenesulfonamides show one irreversible reduction step in the range of - 2.8 to 3.0 V (vs. Ag/Ag^+). Constant potential electrolyses were carried out at the potentials of the voltammetric peaks. It was observed that the addition of phenol has