ADVANCES IN
CHEMICAL PHYSICS

Volume III

ADVANCES IN
CHEMICAL PHYSICS ·

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VOLUME III

INTRODUCTION

In the last decades, chemical physics has attracted an ever increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into

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something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity has been attained — a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

I. PRIGOGINE

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MECHANISMS OF ORGANIC ELECTRODE REACTIONS*

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CONTENTS

I. INTRODUCTION

The primary aim of the present discussion is to summarize current approaches to the problem of the elucidation of the mechanism of the half-cell reaction for the electrolysis of an organic compound at an electrode. This reaction can be depicted in its simplest form as

$$Ox + ne = Red \tag{1}$$

where Ox represents the oxidized form, Red the reduced form and n the number of electrons transferred.

The stoichiometric form of Eq. 1 is usually quite simple, involving simple numerical ratios of oxidized and reduced forms with perhaps the addition of one or more of the species; hydrogen ions, hydroxyl ions and water, to balance the equation. However, the actual course of the reaction is quite complex since it is at least formally heterogeneous in nature, involving electron transfer between presumably a solution species or its adsorbed or otherwise altered form, and the electrode, and occurring in the interfacial region between bulk solution and electrode, which is distinguished as the electrical double layer.

Theoretically and experimentally, we have a relatively good picture of the mass transfer process, i.e., of the process of bringing an electroactive species from a point in the bulk solution "up to the electrode," although the latter phrase is often not too clearly defined in terms of the various subregions of the interfacial region between the physical electrode and the bulk solution. A number of treatments of more or less satisfactory nature have been made of the relations of the rates of the heterogeneous electron-transfer process to the observed potential and current values. (Treatments involving the effect of coupled chemical reactions preceding and following the electron-transfer step or steps have been described, e.g., Koutecký's excellent studies). However, these have not been systematically applied to the situations prevailing in organic electrode reactions. Many studies have been made of the reaction mechanisms of organic electrode reactions. Some of these studies have been very interesting and penetrating, but others have been lessened in value by such factors as generalizations based on data for too few compounds, failure to identify positively the reaction product or products, neglect of the effects of experimental conditions, overly naive treatment of the experimental data, and neglect of the kinetics and energetics of the electron-transfer process.

The further purposes of the present study are to indicate the physical bases and the interrelationships of the treatments of different aspects of organic electrode reactions, and to emphasize

the basis for a synthesis of the various treatments in so far as their presently revealed interrelationships permit this to be done.

The discussion is based primarily on data gathered by polarographic and derived voltammetric and electrolytic techniques and on the interpretations of such data. The use of known potential relations is essential to the interpretation of electron-transfer processes.

II. REACTION MECHANISMS OF ELECTRODE REACTIONS

Currently, three general approaches to the problem of organic electrode reaction mechanisms are being made: (1) The *chemical* reaction mechanism, in which the mechanism is stated in terms of the species involved on the basis usually used in describing organic chemical reaction mechanisms in homogeneous solution. (2) The *electrochemical* reaction mechanism, in which the processes occurring are described from the viewpoint of a more detailed analysis of the physical situation. (3) The *energetic* reaction mechanism, in which a more precise and, if possible, mathematical statement of the relation between the electron-transfer steps and the mechanistic picture is attempted.

In a sense, this sequence is a logical development in the elucidation of a mechanism and its interrelations with the factors involved. The three approaches will be discussed in that order.

Since the electrochemical reduction of organic compounds has been so much more extensively studied than the electrochemical oxidation of such compounds, the discussion will stress reductive processes, although the general ideas involved are equally well applicable to oxidative processes after due allowance is made for the change in direction of electron transfer.

A. Bond Rupture

Electrochemical reduction in the case of an organic compound involves, as in the reduction of an inorganic species, the net transfer of electrons from the electrode to the electroactive species; the essential difference is that in most inorganic reductions "normal" chemical bonds are rarely considered to be broken except, perhaps, in the cases where the electroactive element

either is present as an oxygenated species or has a lesser coordination number in the reduced state than in the oxidized state. On the other hand, organic reductions involve readily observed changes in the structure of functional groups or moieties with the concommitant feature that a single organic electrode reaction involves the transfer to the electroactive species of: (a) one electron, if a free radical is produced which dimerizes at the site of the electroactive moiety or at one derived from it through intramolecular electron rearrangement; (b) two electrons, if a bond is completely severed without formation of an intermediate free radical and its consequent dimerization preceding further electron transfer; or (c) combinations—simultaneous and/or successive—of one-electron and/or two-electron processes.

B. Processes. Involving More Than Two Electrons

The situation has been frequently described in the literature where the overall electrode reaction, e.g., that giving rise to a single polarographic wave, involves the transfer of more than two electrons per molecule of electroactive substance; such electrode reactions are due to either (a) a succession of processes whose potentials are so close together that a single reaction seems to be occurring, or (b) the occurrence of a one- or two-electron process at a certain potential to produce species which would be themselves reducible at a less energetic potential· and which consequently immediately upon formation accept more electrons.
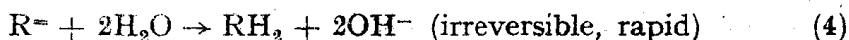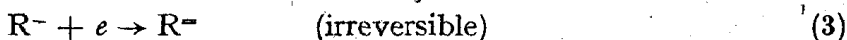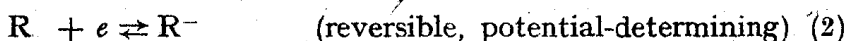
It is reasonable to assume on the basis of the considerable corpus of recent work on the mechanisms of inorganic and organic, homogeneous and heterogeneous (including electrode) reactions, that the occurrence of an electrode reaction involving the "simultaneous" transfer of more than two electrons is practically nil. Indeed, a question might be legitimately raised as to whether the apparently observed "simultaneous" two-electron transfer processes are not actually two one-electron processes which follow each other exceedingly rapidly in time, e.g., within, perhaps, less than either the life-time of an intermediate species or the time of a single molecular vibration. Since the previous argument

often is a nonoperational one and since dimers indicating one-electron processes do occur, we shall assume that a "simultaneous" two-electron process is the rapid succession of the reactions represented by subsequent Eqs. 14 and 18, with the amendment that the electrons may follow each other so rapidly that the transition state effectively represents a combination of the electroactive species and two electrons.

III. CHEMICAL REACTION MECHANISM

The chemical reaction type of mechanism is usually stated in terms of a set of chemical equations, certain ones of which may be specified as being "fast" or "slow" in order to emphasize potential-determining stages in the overall reaction. The only distinguishing characteristic is the treatment of the electron as one of the reactants with the often implied premise that an electron-transfer-step must be the essential or determining stage.

Typical of such schemes is the one originally proposed by Laitinen and Wawzonek[15] to explain their observations on the pH-independent polarographic reduction of styrene and stilbene:

$$R + e \rightleftharpoons R^- \qquad \text{(reversible, potential-determining)} \qquad (2)$$

$$R^- + e \rightarrow R^= \qquad \text{(irreversible)} \qquad (3)$$

$$R^= + 2H_2O \rightarrow RH_2 + 2OH^- \quad \text{(irreversible, rapid)} \qquad (4)$$

Although this model was based on rather meager experimental evidence which has been shown to be—at least in part—insufficient to describe fully the behavior of the compounds involved,[10] the reaction scheme of Eqs. 2 to 4 has been used to explain quite adequately the observed polarographic reduction of many organic compounds. The present discussion is obviously indebted to this pioneering and provocative suggestion.

Many attempts have been made to describe the experimental data in terms of substitution or free radical mechanisms, e.g., references 4 and 7. These mechanism deductions and the tests made of them have been based generally on the correlation of the

ease of reduction with structural factors and products* rather than on kinetic considerations as in the case of homogeneous solution reactions. Such attempts to explain or at least to describe a heterogeneous reaction in terms originally defined for homogeneous solution reactions are certainly open to criticism on that account. However, the success or lack of success of such treatments may help to indicate the extent to which the electrode reaction is explicable in such terms.

In the subsequent discussion, we shall consider the successive stages in the breaking of a bond, e.g., the bond between a carbon atom which can be taken as the reaction center and some other atom Y at the electroactive site, $R'_3C\text{---}YR''_m$, where R' and R'' represent any substituents including C and Y as in the particular cases of multiple bonds between C and Y, and of several Y connected to the same C center, and m is any number, including zero, which is necessary to define the species involved. For convenience, we shall represent the $R'_3C\text{---}$ entity as R and $\text{---}YR''_m$ entity as X with the electroactive species being then written as R---X or, if we assume a localized electron pair to describe adequately the bond, as R : X. Obviously, the reactive center can be an atom other than carbon; nitrogen, oxygen and sulfur have been found, *inter alia*, to function as reactive centers in organic electrode reactions.

The general approaches for the common types of organic reaction mechanisms can be summarized as in the following equations. Hydrogen and hydroxide ions, and water are not being shown except where necessary to indicate the final establishment of an electrically balanced species. The role of such species as reactants in potential-determining reactions is subsequently discussed. A similar statement applied to the situation where a multiple bond exists originally between R and X, and one or more bonds between them persist in the product of a step in the reaction or of the overall reaction.

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* E.g., expected ease of bond fission based on considerations of permanent polarization and polarizability, and compatibility of observed behavior on substitution with that predicted for different types of mechanisms.
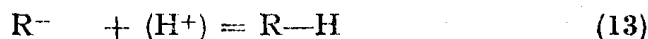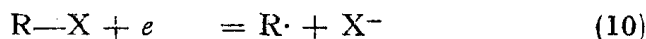
S_N1 process:

$$R{-}X = R^+ + X^- \tag{5}$$

$$R^+ + 2e = R^- \tag{6}$$

$$R^- + (H^+) = R{-}H \tag{7}$$
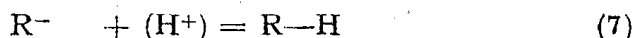
(The species, (H^+), is intended to represent a proton source such as water or hydrogen ion.)

S_N2 process:

$$R{-}X + 2e = R^- + X^- \tag{8}$$

$$R^- + (H^+) = RH \tag{9}$$

Free radical process:

$$R{-}X + e = R{\cdot} + X^- \tag{10}$$

$$R{\cdot} + R{\cdot} = R{-}R \tag{11}$$

$$R{\cdot} + e = R^- \tag{12}$$
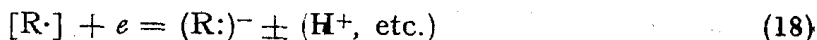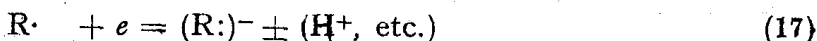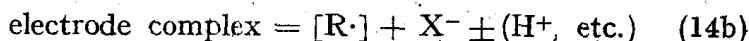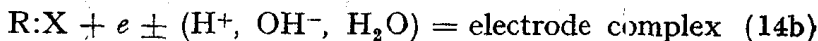
$$R^- + (H^+) = R{-}H \tag{13}$$

Operationally, there is often but little difference between the S_N1 and S_N2 mechanisms. In the use of the S_N1 description, one would like the electron-transfer step to be potential-determining. To do this, it is necessary to assume that the energy-controlling dissociation (Eq. 5) is due to the electrical field, i.e., the electrode potential, and that consequentially the electrons enter simultaneously. However, this is equivalent to the transition state that has to be postulated for the controlling stage of the S_N2 mechanism (Eq. 8). Consequently, it is probably more justifiable to speak of the *ionic* or *carbanion* mechanism, rather than of the S_N1 or S_N2 mechanism.

The ionic mechanism accommodates the data in the following respects: The slow step involves electron attack; there is simultaneous dissociation of the X entity so that the R—X bond strength must be involved in the potential required for reaction.

The free radical hypothesis is even more satisfactory and is considerably more popular. The isolation of dimer products (Eq. 11) is powerful evidence for this mechanism. The potential-determining step is usually assigned to the introduction of the first electron (Eq. 10), which is the step involving bond fission.

A. General Mechanism

A general sequence of reaction steps can be postulated, which will afford a basis for indicating the possibility of both ionic and free radical mechanisms. Such a general mechanism will facilitate the discussion of electrode processes, which, for example, may seem to change mechanism with experimental conditions or between members of a homologous series. The possible overall steps in a reaction occurring at an electrode may then be represented as follows:

$$R:X + e \pm (H^+, OH^-, H_2O) = \text{electrode complex} \quad (14b)$$

$$\text{electrode complex} = [R\cdot] + X^- \pm (H^+, \text{ etc.}) \quad (14b)$$

$$[R\cdot] = R\cdot \quad (15)$$

$$R\cdot \; + R\cdot = R:R \quad (16)$$

$$R\cdot \; + e = (R:)^- \pm (H^+, \text{ etc.}) \quad (17)$$

$$[R\cdot] + e = (R:)^- \pm (H^+, \text{ etc.}) \quad (18)$$

$$(R:)^- + (H^+) = R:H \pm (H^+, \text{ etc.}) \quad (19)$$

$$(R:)^- = \text{electronic rearrangement products} \quad (20)$$
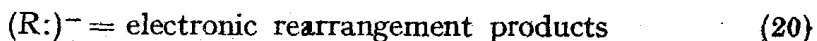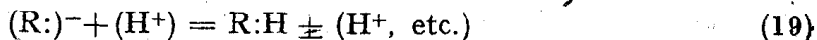
Equations 14a and 14b represent the formation of an electrode intermediate species, $[R\cdot]$, which may be converted to a more or less stable trigonal free radical (Eq. 15) or may be reduced to a carbanion (Eq. 18). The free radical formed may dimerize (Eq. 16) or be reduced to a carbanion (Eq. 17). The carbanion may then neutralize itself by acquisition of a proton from a solvent or interfacial species (Eq. 19) or by intramolecular electronic rearrangement (Eq. 20) with elimination of an anion.

If R and X are connected by multiple bonds, the combined initial reactions (Eqs. 14a and 14b) may be depicted as follows, where each horizontal line conventionally represents an electron pair,

$$R=X + e = [R-X]^- \pm (H^+, \text{ etc.}) \quad (21)$$
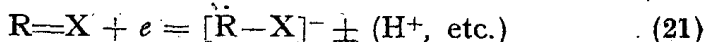
However, since multiple bond reductions frequently, if not always, involve a third reactant, which is a solution component,

Z, such as hydrogen ion, it is probably better to use the following equation

$$R{=}X + e + Z = [\dot{R}{-}X{-}Z] \pm (H^+, \text{ etc.}) \qquad (22)$$
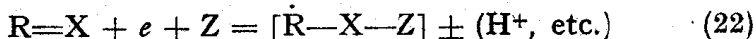
Succeeding reactions of the intermediate species can still be depicted by Eqs. 15 to 20.

The general mechanistic scheme described will obviously be applicable to situations such as those which led to the mechanism proposed by Laitinen and Wawzonek[15] which has been described, as well as being a more general formulation of the mechanism model used by Evans and Hush[9] to interpret ionogenic reactions involving bond breaking at electrodes.

Certain qualifying and characterizing statements might be made about the proposed reaction scheme. For example, relative to the involvement of hydrogen (or hydroxyl) ion in the reactions as an energy-controlling component, the reaction of Eq. 19 is generally so rapid that it is not potential-controlling. It is safe to say on the basis of the many observations made on reactions whose potentials are pH-dependent, that such pH-dependence is commonly associated with the reaction of Eq. 14; there are few, if any, well-defined examples of the reaction represented by Eqs. 15 to 18 being pH-dependent. For example, in reductions such as those of ketones where two polarographic waves are observed with the first wave due to formation of a free radical species and the second to the reduction of the latter, the first wave may be pH-dependent but the second wave apparently never is. Such pH-dependence of the first wave may then be associated with hydrogen or hydroxyl ion being involved in formation of the energy-determining activated complex or transition state, whether the hydrogen or hydroxyl ion is involved in the final stoichiometry of the first step as in Eq. 22 or is not (Eq. 14, disregarding items in parentheses). This does not necessarily mean that every first reaction step representable by Eq. 22 is pH-dependent.*

However, this does not affect the principles of the text

* The importance of hydrogen ion in determining the state of the electroactive species involved and consequently the energy of the reaction is considerable in many situations, e.g., those involving acid-anion and keto-enol systems.

discussion. For example, the half-wave potential of the 2-bromoalkanoic acids is pH-dependent in the pH region where the shift from anion to more readily reduced acid form may be expected to be appreciable; the fundamental carbon-bromine bond fission process is pH-independent throughout the pH range involved.

The argument is a general one, since other solution components in addition to hydrogen ion may affect the reactive species; e.g., the studies of Zuman and Brezina on the effect of ammonia and amines on carbonyl group reductions. An analogous argument concerns the effect of possible ion pair formation between, e.g., a carbanion and a metallic cation.

Operationally, then, the chemical reaction mechanism for an organic electrode reaction can be summarized as follows (cf. Fig. 1):
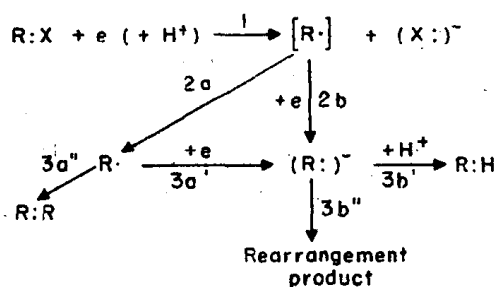

Fig. 1. Generalized chemical reaction mechanism. The initial reaction product may be, if R and X were connected by multiple bonds, [Ṙ—X—Z].

The initial step in the reaction is the addition of an electron to the electroactive species with hydrogen ion participating in this step if it can aid the process by chemical polarization of the R—X bond through formation of a more or less stable H—X bond (hydrogen ion is used in this discussion since it is the most common third participant in the initial step, although other species, e.g., another Lewis acid, may act similarly). This initial, generally potential-determining step is followed by step 2a or