

ORGANIC SEMICONDUCTORS

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Preface

The remarkable growth of interest in the physics and chemistry of the organic solid state is reflected by a steady increase in the number of published investigations dealing with various aspects of this subject. Research on the organic solid state is increasingly being recognized as an interdisciplinary field of study which combines related work not only by chemists and physicists but also by electrical engineers, biologists and even medical researchers. While some of the initial impetus for such research has no doubt been stimulated by the progress which has been achieved from the study of the solid state properties of inorganic materials, particularly as related to semiconductivity phenomena and their practical utilization, organic solid state science has now made enough strides to stand on its own feet, so to speak. The theoretical and practical consequences of studies of the organic solid state can as yet not be clearly ascertained, and they may not necessarily follow the route set by the inorganics. It is proper to expect however that a better understanding of the organic solid state will give us, at the very least, increased insight not only into the electronic properties of organic solids but also into energy conversion systems, luminescence and even certain biological processes.

The rather diffuse nature of this very broad subject has prompted the publication of pertinent investigations in a great number of different journals not all of which are those routinely perused by chemists and physicists. This has made it difficult for the individual

researcher interested in this field to maintain adequate contact with all of the important developments. Because of this, the authors have decided to offer the subsequent survey of organic semiconductors which, it is hoped, will tie together much diverse and apparently unrelated work into some sort of order and coherence. This present book should then be considered as a progress report rather than a definitive treatise—a progress report reflecting recent research and its difficulties in an admittedly very complex field. Because of the authors' background, the point of view taken throughout has been that of the chemist rather than the physicist. Photoconductivity, an admittedly very important subject related to the study of the organic solid state, has not been discussed, both on account of its far reaching implications which encompass such matters as photosynthesis and for reasons of space; it is felt that photoconductivity well deserves a separate study. This book, therefore, is centered on an account of research on the dark conductivity characteristics of organic solids and their manifold effects on the properties of organic materials.

It has obviously been impossible to review and give credit to every reported investigation; much effort has been exercised however to include all of the important references up to early 1963. Because of the fast-moving nature of this field, however, certain specific important work may not have been credited; in all such cases the authors acknowledge their fault and ask for understanding.

As with any work of this type, the authors would like to acknowledge the cooperation and help of the many individuals without whom this book could not have been completed; it is a special pleasure to thank Dr. A. F. Armington, U.S. Air Force Cambridge Research Laboratories, who prepared the chapter on the Electronic Properties of Carbons, Drs. M. Pope and Y. Matsunaga who commented on sections of the book; Dr. M. Sano who read this book in its entirety and made valuable suggestions; and Mrs. A. Gordon who performed the formidable task of preparing the entire manuscript.

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1

Introduction

The vast number of chemicals which are conventionally classified within the province of organic chemistry are generally considered in terms of electrical insulators. In recent years, however, an increasing number of organic compounds has been discovered to exhibit pertinent electrical characteristics which do not fit this concept.^{1,2} The term "organic semiconductors" has been used to describe organic solids which contain a significant amount of carbon-to-carbon bonding but show some capability of supporting electronic conduction.^{3,4} A common factor in all definitions is the employment of the property of electrical resistivity as a distinguishing material characteristic. It is customary to consider organic semiconductors as materials which exhibit electronic conductivities in between those of metals (10^4 to 10^6 ohm⁻¹ cm⁻¹) and insulators (10^{-22} to 10^{-10} ohm⁻¹ cm⁻¹), that is the broad range of 10^{-9} to 10^{+8} ohm⁻¹ cm⁻¹.

Semiconducting organic solid materials are frequently grouped into the categories of molecular crystals, charge transfer complexes, and polymers. Molecular crystals such as naphthalene and anthracene are among the most thoroughly studied organic compounds. Very low resistivities have been measured on diverse charge transfer complexes, the further investigation of which may have important implications for biological systems. Polymers including the so-called pyropolymers are being extensively investigated with em-

phasis on conjugated long chain structures. The primary aim of current research is to obtain a better understanding of the mechanisms of electron transfer in molecular solids and the relation of such mechanisms to the physicochemical structures of such solids. Research in organic semiconductors is carried out mainly at the basic level but has created much interest in various industrial organizations, particularly those interested in solid state properties.

Historically the study of the electronic conductivity of organic solid compounds may be traced back to the beginning of this century. The discovery of the photoconduction of solid anthracene was described by Pochettino in 1906.⁵ Koenigsberger and Schilling demonstrated the existence of a small but measurable dark conduction in anthracene.⁶ A number of additional papers was published, but by 1914 interest in this field had almost completely lapsed—a situation which was to prevail for almost twenty years.

Some experiments were carried out in subsequent years on the problem of photoconduction in certain organic dystuffs. Vartanyan was particularly interested in the part which photoconduction plays in the sensitization of photographic emulsions and published extensively in this area.^{7,8,9} Electronic excitation of the dystuff molecules followed by transfer of an electron to the silver halide was considered to be an important step of the sensitization process. A recent review of this field has been published.¹⁰

Szent-Györgyi is generally credited with having helped to revive the study of organic semiconductors by publications in 1941 in which he suggested that the transfer of π electrons from molecule to molecule may play an important role in the fundamental processes of biological systems.^{11,12} Photoconduction of certain dyed proteins was reported by Szent-Györgyi in 1946 as evidence for the validity of his original proposition.¹³ The significant revival of interest in organic semiconductors is reflected by a steadily increasing number of papers on the subject of conduction and photoconduction in organic materials in subsequent years. Of special interest is the discovery in 1948 by Eley of the exponential variation of the conductivity of certain phthalocyanines with the reciprocal of the temperature, which relationship was later found to be equally applicable to various other organic compounds.¹⁴ Photosynthesis was related to organic semiconductivity by Katz,¹⁵ Bradley,¹⁶ and

Calvin.¹⁷ Semiconductivity has been connected to carcinogenesis by Pullman and others.^{18,19}

The demonstration of the remarkably low conductivities which are exhibited by certain charge transfer complexes, as shown by Akamatu, Inokuchi, and Matsunaga in 1954, marked yet another milestone in the study of organic semiconductors.^{20,21} Many other charge transfer complexes have since then been shown to possess semiconductive behavior.^{1,2} Polymeric phthalocyonines have been studied by Wildi and Epstein.²² Recent reviews have indicated the major types of organic polymeric semiconductors studied to date.^{23,24,25} Research in organic semiconductors is now proceeding at a much faster pace stimulated in no small measure by the remarkable technological progress which was achieved with silicon, germanium, and other inorganic semiconductors.

It has been noted above that the major aim of current investigations is the better understanding of the nature of the electron transport processes in molecular solids especially as related to their physicochemical structure. There exists, however, an exciting practical potential as well. The organic chemist having at his disposal over 900,000 different organic compounds and considerable synthetic skills may be able to tailor make semiconductor materials with properties exactly matched to the requirements of specific applications. Thus, fabricators of electronic devices can conceive of completely new films, filaments and molded shapes specially prepared to best suit particular purposes. Furthermore such novel products have the additional promise of lower materials costs and more ready fabricability compared to inorganic semiconductors. While it is too early to attempt to predict the future development of this exiting new discipline, the rapid progress which is being made now augurs well for the future. There is considerable basis for the confidence of the chemical industry to be able to convert the basic research results now being developed, into useful industrial products in application potentials ranging from thermoelectricity to sea water desalination. When the character of electronic conductivity in molecular solids is better understood, basic life processes such as photosynthesis and cell conditions may also be better explainable and, hence, controllable.

The accomplishment of these tasks is a large order indeed. The

combined efforts of the organic, physical, and polymer chemists, as well as of physicists, mathematicians, and medical researchers, will be necessary to arrive at satisfactory solutions. It is certain that, regardless of what will be learned about organic semiconductivity in the laboratory, new and important developments in almost any area of knowledge will spring from such basic studies. It is this belief which has made this field so attractive to both science and industry.

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2

Electronic Conduction Mechanism in Organic Materials

The spectacular advances which have been made in the theory, preparation, and applications of inorganic semiconductors, such as silicon and germanium, have no doubt accelerated analogous investigations of the conduction mechanism in organic materials. Investigations of organic semiconductors have tended to confirm the existence of such compounds and increasingly emphasize the close relationship between the physics and chemistry of semiconductors. Thus, a full understanding of either area can be gained only by considering the relation between them. Today it is already possible to prepare organic solids with a very wide range of electronic properties, although an adequate understanding of the mechanisms of conduction is still lacking. It is the purpose of this chapter to describe some of the theoretical concepts which have been advanced for a better understanding of the many and often isolated experimental facts observed to date.

From a chemical point of view the better organic conductors have been classified as compounds which have a number of delocalized electrons (π electrons) in the molecules, free radicals, and charge transfer complexes. Although considerable experimental work has been carried out on the preparation and the study of the electronic properties of these materials, no comprehensive theory of the conduction mechanism in organic solids has as yet been proposed. A principal reason for this state of affairs is the fragmentary

and generally less than satisfactory knowledge of intermolecular interactions in the solid state.

The most widely used explanation of the experimentally observed conduction phenomena of organic solids is in terms of a modified electronic band model of these solids. This is essentially a quantum mechanical approach involving the calculation of the width of energy bands by calculating overlap integrals between π electron molecular wave functions on adjacent molecules. The relative weakness of the intermolecular attractions in molecular crystals results in rather narrow conduction bands and low carrier mobilities. A summary of this approach which, while admittedly imperfect, may help in the analysis and evaluation of experimental data follows.

When the temperature of organic crystals is increased to a suitable degree, thermal excitation will occasionally raise an electron from the ground state to the excited conducting state. Thus, a "hole" is created as well as a conduction electron. The processes of thermal excitation and recombination of electrons and holes continue until a dynamic equilibrium is established. This state is characterized by a time independent electrical conductivity. By raising the solid to a sufficiently high temperature, any insulator can be expected to show this type of behavior, which has been called "intrinsic" semiconduction since it is an intrinsic property of the material. The process corresponds to a thermal excitation across the forbidden gap, from the valence band to the conduction band. The temperature necessary to develop intrinsic semiconduction is a function of the width of the forbidden energy gap (Figure 2-1).

For materials containing impurities, the electronic conductivity may be controlled by the impurities. Such behavior is called "extrinsic" semiconduction, as it depends on the nature of the impurities and the concentration of imperfections in the crystal lattice. However, very little is known about the role of impurities in the organic semiconductors.

For inorganic semiconductors, boron in germanium offers an example of an extrinsic semiconductor in which an excess of holes has been introduced. Semiconductors which have an excess of holes over conduction electrons are called "*p*-type," because their conductivity arises from the presence of positive current carriers.

Those with an excess of electrons are called "n-type" since the carriers are negative. The current carriers are called majority or minority carriers depending on which predominate. A semiconductor in its intrinsic range has equal concentrations of holes and electrons, as discussed above.

When the energy gap is expressed by ϵ , the concentration of the current carriers (holes and electrons) should then vary with temperature according to the following relationship:

$$n = n_0 \exp(-\epsilon/2kT) \quad (1)$$

where k is Boltzmann's constant and n_0 is a constant. ϵ is the difference in energy between the highest point in the valence band and

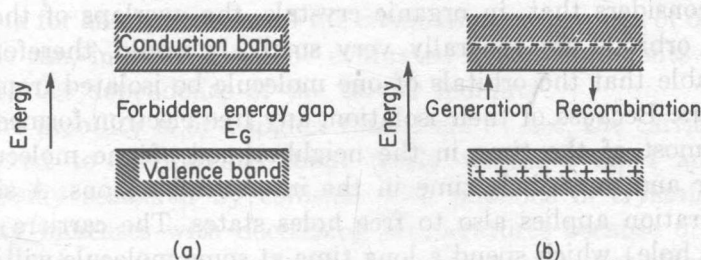


Figure 2-1. Intrinsic semiconductor, (a.) at low temperature, (b.) at elevated temperature, with thermal excitation generating holes and conduction electrons.

the lowest point in the conduction band. The factor of $\frac{1}{2}$ in the exponent appears with intrinsic semiconductors because the possible distributions of electrons in the conduction band are independent of the distributions of holes in the valence band. Then, the conductivity may generally be expressed as follows:

$$\sigma = |e|(n_n\mu_n + n_p\mu_p) \quad (2)$$

where n_n is the density of electrons, n_p is the density of positive holes, μ_n and μ_p are the mobility for electron and hole.

If it is assumed that the mobility of the carrier varies rather slowly with temperature,¹ Equation (1) may be then rewritten for the experimental conductivity as follows:

$$\sigma = |e|(\mu_n + \mu_p)n_0 \exp(-E/kT) \quad (3)$$

and

$$\sigma = \sigma_0 \exp(-E/kT) \quad (4)$$

where σ_0 is a constant and $E = \frac{1}{2}\epsilon$. In this equation the energy term is one of the most important factors for the study of organic semiconductors.

A number of authors assume that the dark conductivity of organic crystals is indeed conventional intrinsic semiconductority, and they use ϵ as the band gap of such crystals. The observed values of ϵ and E_i are almost equal leading to the further assumption that the molecular triplet state is involved in the conduction.² However, the validity of this assumption was criticized by Fox who advocates the following point of view.^{3,4}

He considers that, in organic crystals, the overlaps of the molecular orbitals are generally very small. It would, therefore, be reasonable that the orbitals of one molecule be isolated from that of others. Because of their isolation, any free electron formed may spend most of the time in the neighborhood of one molecule or another and very little time in the interstitial regions. A similar consideration applies also to free holes states. The carriers (electron or hole) which spend a long time at some molecule will jump to a neighbor's molecule by the perturbations arising from the presence of other molecules (hopping model).

Examples of such conduction mechanisms can be found in inorganic semiconductors such as NiO and Fe₂O₃. In NiO, for example, the overlaps of the 3*d* orbital in Ni⁺⁺ are very small; and the 3*d* band in Ni is only $\frac{1}{15}$ as wide as the 4*s* band. The narrowness of the band implies a high effective mass and low carrier mobility in the band. The mobility at 300°K is 0.004 cm²/V-sec and increases exponentially with temperature, with an activation energy of 0.1 eV. Conduction in NiO and Fe₂O₃ by the above mechanism presumes that a potential barrier exists which must be overcome to enable a charge carrier to jump from one location to another.⁵

To find the excitation energy for the lowest conducting state for the hopping model or the band model,⁶ the charge transfer mechanism is considered to occur in several steps. The electron is first removed from its original molecular location to a point far

from the crystal; this requires the ionization energy E_I . Bringing the electron back to the crystal and placing it on the second molecule involves the electron affinity energy E_A . If the ion pair is widely separated, each ion will polarize the surrounding molecules. The energy, W , of interaction of each ion with the polarization is identical for the two ions, as a first approximation. The excitation energy is then $E_I - E_A - 2W$. There are other considerations, but they are small in effect compared with those considered above.

Either the electrons on the negative ions or the hole left behind on the positive ions can carry current by hopping to adjacent molecules. The two charges are sufficiently far apart that they act independently of one another.

The applicability of either the band model or the hopping model concepts for an explanation of the conduction mechanism of organic crystals can, in some cases, be evaluated by measurements of the temperature dependence of the carrier mobility.

If the mobility is of a higher than $1 \text{ cm}^2/\text{V-sec}$, the carriers are considered to be moving about freely within a band and are periodically scattered by collision with phonons in crystals. The mobility increases with decreasing temperatures because of a decrease in the number of phonons or scattering centers. However, if the mobility is less than $1 \text{ cm}^2/\text{V-sec}$, it seems more reasonable to consider the localization of the charge carriers on particular lattice sites. Recently Kepler has reported on mobility measurements in anthracene.⁷ He found that the mobilities were in the order of $1 \text{ cm}^2/\text{V-sec}$ and also that they are anisotropic (see Chapter 3). The calculated values by LeBlanc are in quite good agreement with these experimental data.^{8,9}

Thus, the transport mechanism of holes and electrons in anthracene can be described with a band model. However, the band model need not be necessarily applicable to other systems, particularly so if the following anthracene experimental restrictions are obviated:⁹

- (a) the material under study exhibits a periodic lattice;
- (b) the carrier concentrations are so small that carrier interactions can be considered negligible.

In liquid hexane the mobilities of photoelectrically injected electrons are quite small ($10^{-3} \text{ cm}^2/\text{V-sec}$) and exhibit the Arrhenius

temperature dependence.¹⁰ The mechanism of transport is not yet clear, but one possibility is that, upon melting, a band model mechanism may be replaced by a hopping model mechanism. This may also be true in amorphous polymeric materials.

The increased number of investigations dealing with the phenomena of electronic conductivity in organic solids offers a real hope for adding substantially to our understanding of the more relevant parameters pertaining to the conduction mechanism. However, much more experimental work is indicated on such problems as measurement of material purities, determination of carrier types and mobilities, ionization energy values, and electrode and temperature effects for various materials of interest.

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