

# TECHNIQUES OF CHEMISTRY

VOLUME III

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## PHOTOCHROMISM

*Edited by*

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# TECHNIQUES OF CHEMISTRY

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VOLUME III

PHOTOCHROMISM

# TECHNIQUES OF CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

## VOLUME I

**PHYSICAL METHODS OF CHEMISTRY**, in Five Parts

(INCORPORATING FOURTH COMPLETELY REVISED AND

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## VOLUME III

**PHOTOCHROMISM**

*Edited by Glenn H. Brown*

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## INTRODUCTION TO THE SERIES

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Techniques of Chemistry is the successor to the Technique of Organic Chemistry Series and its companion—Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can easily be recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

Authors and editors hope that readers will find the volumes in this series useful and will communicate to them any criticisms and suggestions for improvements.

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ARNOLD WEISSBERGER

## PREFACE

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W. Marckwald in 1899 gave the name "phototropy" to the reversible process in which a solid changes color when exposed to visible light and reverts to its original color in the dark. Since this early observation scientists have found that the phenomenon includes other states of matter and that exciting radiation need not be limited to the visible region of the spectrum. In recent years the name "photochromism" has been assigned to the phenomenon. This term is composed of two parts: *photo* (light) and *chrom* (color). The suffix "ism" indicates a phenomenon.

From its discovery photochromism has been associated with reversible, light-induced photochemical processes that result in a color change. We now look on the photochromic phenomenon as a reversible change of a single chemical species between two states having distinguishably different absorption spectra, such change being induced in at least one direction by the action of electromagnetic radiation.

This book can serve as a source of reference and as a text. As a reference book it can be turned to for the clarification of a given point or for the details of some important experiment. On the other hand, it is an explanatory text that deals with principles.

The literature on photochromism has grown rapidly during the past decade. Both the scientific and patent literatures have been reviewed and critically analyzed. The reader will find an up-to-date survey of "the state of the art" which can serve as a starting point for initiating research programs.

Photochromism was first described in scientific literature in 1876, but there was little research on the subject until about 1920. From 1920 to 1930 there was a serious study of the subject, but most reports were of a qualitative nature. Interest in photochromism lagged in the 1930s whereas the period from 1940 to 1960 saw a revival of interest in the field. Many new compounds were prepared, both organic and inorganic. Many scientific advances were made including mechanisms to explain different photochromic processes and structural determinations of reactants, products, and intermediates.

In the past ten years the study of photochromic materials has been rather popular. In addition to the scientific interest in the subject, there has been considerable commercial interest. In fact, much of the fundamental research on photochromism has been done in industrial laboratories.

The chapters in this book focus attention on the developments during recent years and also place earlier studies in their proper perspective. On checking the Contents the reader will see that the heart of the book is concerned with photochromic processes which have been well documented. These processes are classified on the bases of their mechanisms. The mechanisms considered are heterolytic cleavage, homolytic cleavage, *cis-trans* isomerism, tautomerism, and the development of color centers in inorganic compounds. In addition to these mechanistic processes the reader is introduced to the fundamental principles of photochromism and to such applied aspects of the subject as photochromic glasses, the use of photochromic materials in self-developing photography, data displays, photochromic microimages, decorations, temperature indicators, and Q-switches. The photochromic phenomenon in living systems is discussed for such processes as photosynthesis and vision.

I wish to thank the contributors for their fine cooperation, understanding, and concern, without which this book could not have been written. To all others who have aided in bringing this book to completion, I owe my deepest appreciation.

*Kent, Ohio*  
*January 1971*

GLENN H. BROWN



# TECHNIQUES OF CHEMISTRY

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VOLUME III

PHOTOCHROMISM

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## INTRODUCTION

Glenn H. Brown

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### 1 HISTORICAL INFORMATION

Marckwald [1] gave the name phototropy to the phenomenon in which a solid changes color when exposed to light but reverts to its original color in the dark. He concluded that, “the action of light described here is purely a physical phenomenon; my reason for describing it is to encourage physicists to investigate the matter further.” Even though the term phototropy was used in the early history of the field, it is not a proper one to identify the phenomenon discussed in this book. The word literally means turning toward light, and it has been used with this meaning by botanists, biological scientists, and biochemists for many years to describe a tropistic behavior of plants.

A more desirable and descriptive term for the subject of this book has evolved in recent years. This term is photochromism, and it is made up of two parts: photo (light) and chrom (color); the suffix “ism” indicates a phenomenon. Photochromism literally means a coloration by light.

In the scientific literature, it appears that the first person to observe photochromism was ter Meer [2], who showed that the potassium salt of dinitromethane changed color when exposed to exciting radiation. Another early contribution to the field of photochromism, published by Phipson [3], concerned the strange case of the painted gate post that appeared black all day and white all night. The gate post described by Phipson was located at the home of a friend. When the behavior of the paint was called to the attention of the manufacturer, he pointed out [4] that he had known of the color

change for ten years prior to Phipson's report. The paint was described by the manufacturer as a "new pigment having a zinc basis." To our best knowledge, the paint was comparable in composition to what we now know as the pigment lithopone.

Before 1900 there were few significant studies of photochromic substances. Marckwald [1] first recognized that photochromism was a new phenomenon and considered it to be a truly reversible photoreaction. Among the first organic compounds tested by Marckwald were benzo-1-naphthylridine (listed as anhydrous quinoquinoline hydrochloride) and tetrachloro-1,2-ketonaphthalenone. Wislicenus [5] noticed the photochromic character of benzalphenylhydrazone. Biltz [6-8] also observed the photochromism of benzalphenylhydrazone and certain osazones.

The early literature cited in the preceding paragraphs foreshadows the work carried out in the first active period of serious research in the field. This period covered about 20 years in the early 1900s, with most of the studies carried out in Italy and India. The studies were concerned primarily with synthesis of materials and observations of such factors as the kind of exciting radiation required, speed of excitation, decay time, fatigue, and conductivity. The early investigators did not, in general, concern themselves with such fundamental questions as those involving the mechanism of a photochromic process and the concomitant energy relationships.

Interest in photochromism in the 1930s was quite limited. It will be sufficient to cite a few advances that were made in this period of time. During this decade mechanisms of a few systems were proposed. Harris et al. [9] suggested that the photolysis of malachite green leucocyanide in an ethanol solution that contained a little water went through ionization and then hydrolysis to form the carbinol. Calvert and Rechen [10] later confirmed the quantum yield. Gheorghiu [11-13] interpreted the photochromism of semicarbazones as an effect of mesomerism and suggested that the change is caused by a displacement of  $\pi$ -electrons, which results in the formation of one or more polar structures. He further proposed that substituents in the benzene ring capable of resonance should favor photochromism, whereas nonresonating substituents would tend to subdue it.

The period from 1940 to 1960 saw a revival of interest in photochromism. These efforts do not match those in many other fields, but the quantity of research showed marked increases over previous periods. Many new compounds were prepared, both organic and inorganic. Different mechanisms were proposed to explain different types of photochromism. More careful studies were made of fatigue characteristics, rates and mechanisms of photochromic processes, structure of reactants, products and intermediates as determined by x-ray, spin resonance, and other instrumental methods. The

research group of the late Y. Hirshberg and his colleague E. Fischer initiated a far-reaching and significant program during this period.

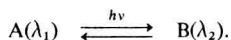
Since 1960, research in the field has shown steady growth. There were conferences in 1962 at Duke University, Durham, North Carolina, and at the University of Dayton, Dayton, Ohio, in 1967 on reversible photochemical processes, with considerable emphasis on photochromic systems. The chapters that follow will focus attention on developments during recent years as well as placing the earlier studies in their proper perspective. Photochromic glasses, the first major photochromic product for the consumer, became available in this period.

A number of review articles [14-23] have been written outlining the development of photochromism since its discovery in 1876.

## 2 DEFINITIONS

When it was first observed, photochromism was associated with the reversible, light-induced photochemical processes that result in a color change. However, we know from recent research that the phenomenon is exhibited over a spectral range wider than the visible region.

In this book, photochromism is defined as a reversible change of a single chemical species between two states having distinguishably different absorption spectra, such change being induced in at least one direction by the action of electromagnetic radiation. This definition can be represented by the following equation:



The inducing radiation, as well as the changes in the absorption spectra, are usually in the ultraviolet, visible, or infrared regions. The change in one direction is thermally induced and usually occurs spontaneously. The process (e.g., *cis-trans* isomerism, homolytic cleavage) responsible for the change in the absorption spectrum is immaterial if the reversibility criterion is met. Irreversible changes represent ordinary photochemistry.

The single chemical species A may be a molecule or an ion. The product B may be a single chemical species also, or it may represent more than one species, provided that they recombine to give A. Thus B may be the *cis* form of *trans*-A; the dye cation and cyanide anion from a triarylmethane leucocyanide; or the radicals from  $\beta$ -tetrachloroketodihydronaphthalene. It may also represent a color center in an inorganic solid formed by trapping of free carriers.

There may be a metastable, ground state intermediate between A and B; for example, an ion pair that disintegrates into the observed ions. One may

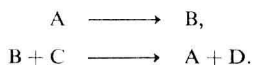
then ask whether the term photochromism should apply to just the first step or to the overall process observed. The answer is not yet clear.

Normally B is in its ground electronic state. An electronically excited state usually fluoresces, phosphoresces, converts its energy to heat, or undergoes irreversible chemical change to something other than A. However, if B is a long-lived triplet (e.g., from a polynuclear aromatic A), it has its own characteristic triplet-triplet absorption spectrum, and the system meets the definition of photochromism. Photochromism involving triplet-triplet absorption will not be discussed in detail in this book; however, some practical applications of it are mentioned in Chapter X.

Commonly, state B, the thermodynamically less stable state, is more deeply colored than is A. This is not necessarily so, however; for example, the colored 15,16-dihydropyrene derivatives decolorize upon irradiation and then thermally revert to the colored form. The same is true of some spiropyrans.

The definition of photochromism says nothing about the rate of the forward reaction; the reversion  $B \rightarrow A$ ; or the spectral regions involved. The reversion  $B \rightarrow A$  occurs thermally and it can also occur photochemically; this is not uncommon among the spiropyrans. Almost all early reports of photochromism were observations of the effect of sunlight during the day and a reversal during the night; the changes were readily visible. Only recently has equipment been available to provide intense radiation anywhere in the spectrum, from infrared to far ultraviolet, to measure absorption changes anywhere in this span and to follow extremely rapid or extremely slow changes in absorption spectra.

The definition of photochromism in terms of a single chemical species excludes reversible chemical processes operating through a cyclic series of reactions illustrated as follows:



In this process, compound A is converted to B by irradiation and then compound B reacts with compound C to regenerate compound A and also a new chemical, compound D. A classic example of a cyclic process is the photoreduction (bleaching) of methylene blue with iron(II) ion and its subsequent oxidation (recoloration) by air. The distinction between photochromism and other reversible photochemical processes must be kept in mind.

Figure 1.1 shows the typical response of a photochromic compound A to activating radiation. Initially the system contains only the A state of the molecule. At time  $t_1$ , the exciting radiation is turned on, producing the colored form, which increases the ratio of B to A molecules. The concentration of B builds to a limiting value with time until the steady state for the equilibrium  $A \rightleftharpoons B$  is reached. If, at time  $t_2$ , the exciting radiation is removed, the colored

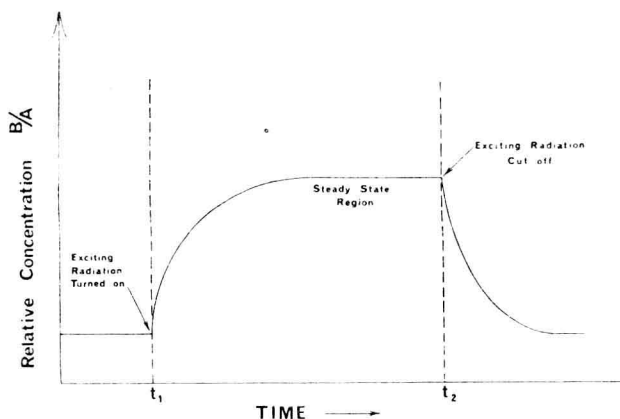
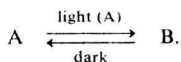


Fig. 1.1 Graph representing typical behaviour of a photochromic substance A:



form B reverts to form A at a rate dependent on the kinetics of the dark reaction.

Photochromic behavior is kinetic. Considering the A-to-B conversion, one finds that only certain wavelengths of radiation will excite A. According to Einstein's photoequivalence law, each quantum absorbed by the photochrome creates an excited molecule. The Grotthuss-Draper law says that only the radiation that is absorbed can produce a chemical change. The number of photons absorbed is controlled by such factors as concentration and extinction coefficient of the photochrome or the wavelength of the exciting radiation, length of the cell, and screening and absorption coefficients of other components (e.g., solvent) in the system. The exciting radiation must be of sufficient energy to activate the photochromic species so that it will pass over the most favorable minimum energy barrier during conversion of A state to B state. All excited molecules may not undergo the conversion to the B state, so the quantum yield is generally less than one. The quantum loss may be attributed to deactivating processes for the activated molecules such as fluorescence, phosphorescence, conversion to heat, and permanent chemical change.

The important characteristics of a photochromic system include the absorption spectra and the extinction coefficients of the parent compound and the photoproduct, the quantum yield of the forward reaction, the occurrence of photochemical reactions instead of or in addition to thermal back reactions, the occurrence of side reactions, and the effect of environmental factors such as solvent and temperature.

One other governing factor will be mentioned, namely, the nature of the



reverse reaction, that is, conversion of B to A. The concentration of the colored form at the steady state is largely dependent on the intensity of the exciting radiation, the temperature, the kinetics of the reverse reaction, and the influence of the solvent on the reverse and forward reactions.

The kinetics of the reverse reaction are generally first or second order. Most reverse reactions are thermally sensitive and a few are speeded up by selected radiation. It is generally believed that the reverse reaction proceeds by a "transition" state of energy higher than that of either the A or B state. All these items and others related to characteristics of photochromic systems are discussed in Chapter II.

### 3 PHOTOCHROMIC PROCESSES

Photochromism occurs in a wide variety of materials, including both inorganic and organic compounds. Illustrative of the classes of organic compounds are the anils, disulfoxides, hydrazones, osazones, semicarbazones, stilbene derivatives, succinic anhydrides, camphor derivatives, certain dye derivatives, *o*-nitrobenzyl derivatives, syndrones, and spiro compounds. A rather large variety of inorganic compounds show photochromism, including metal oxides, alkaline earth metal sulfides, titanates, mercury compounds, copper compounds, certain minerals, and transition metal compounds such as the carbonyls.

The organic materials, both as solids and in solution, are activated almost exclusively by ultraviolet light in the usual range of 200 to 400 nm. For some organic materials, this range may be extended to approximately 430 nm, these materials thus being activated in the blue region of the spectrum. Very few organic photochromic materials are converted from the more stable to the less stable form by visible light, even when the energy difference between the forms corresponds to the energy of visible light. Crystalline inorganic solids, however, may be activated by wavelengths anywhere in the spectrum, ranging from infrared to x-ray to gamma rays, although, again, ultraviolet activation is most common. This wider range of spectral sensitivity is caused partly by the involvement of different mechanisms, such as *F*-center formation and photoionization, and partly by the importance of the crystal lattice in determining the energy levels of the solid.

The absorption of the irradiated form of organic materials in solution or in the solid state may be in the ultraviolet region, as is often the case in *trans* → *cis* isomerizations of simple olefinic compounds. Absorption in the visible region of the spectrum is the readily observable and more common case of photochromism. Only rarely is the absorption in the infrared region, since most organic compounds do not have a structure that can lead to a strong electronic transition in the infrared. Infrared absorption may be expected in