



The Chemistry of Excitation at Interfaces

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J. Kerry Thomas

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The Chemistry of Excitation at Interfaces

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FOREWORD

ACS MONOGRAPH SERIES was started by arrangement with the interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July 1919, when the American Chemical Society undertook the production and publication of Scientific and Technological Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors and associates to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted. Since 1944 the Scientific and Technologic Monographs have been combined in the Series. The first Monograph appeared in 1921.

These Monographs are intended to serve two principal purposes: first to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science; secondly, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs give extended references to the literature.

ABOUT THE AUTHOR

J. KERRY THOMAS earned his doctorate in 1957 from the University of Manchester, England. He was awarded an Honorary Doctor of Science at Manchester in 1969, and the Research Award of the Radiation Research Society in 1974. He developed pulse radiolysis and laser-flask photolysis studies while at Harwell in England and Argonne National Laboratory in Illinois. He is presently the Father

Julius A. Nieuwland, C.S.C., Professor of Science at the University of Notre Dame. His interests lie in radiation and photochemistry, in particular fast-pulsed methods, in the chemistry of surfaces, and in colloidal systems.



PREFACE

ADVANCES IN BIOCHEMISTRY and biophysics have encouraged more chemists to direct their attention to these areas of research. Perhaps two areas of study stand out: the role played by organized assemblies such as membranes or enzymes in controlling material transport and catalysis selection reactions, and the role played by such assemblies in the interaction of light, as in vision or photosynthesis.

Direct chemical and physical studies usually are made *in vivo* or on extracted parts of the organism. However, it is also possible to start with simple chemical systems and by gradually increasing their complexity, arrive at model systems that provide information to the biologist. This text deals with the latter approach to colloids. Their structure and the role that they play in radiation-induced reactions are investigated.

I would like to thank T. Gautier, J. English, and P. McCormack, for converting my hand-written text into something that could be read by others. I would also like to thank my research group T. Wheeler, J. Kuczynski, R. Stramel, P. Hite, D. Chu, S. Hashimoto, and T. Nakamura for checking the manuscript. The inspiration for the text is due to those who provoked and guided me over the years, the late J. H. Baxendale, J. L. Magee, M. Burton, and E. J. Hart.

I would also like to thank various research agencies who have supported my work over the years: the U.S. Atomic Energy Commission, for studies in radiation chemistry; the National Science Foundation, for photochemistry and micellar studies; the Army Research Office, for studies in inorganic colloids; and the Petroleum Research Fund of the American Chemical Society, for helping me start many important projects.

The text is dedicated to that greatest of all organized assemblies, my family: Ronald, Rebecca, June, Delia, Roland, and Roger.

J. KERRY THOMAS

University of Notre Dame
Notre Dame, Indiana

January 1984

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Introduction

MUCH OF THE CHEMISTRY TAUGHT TO STUDENTS, or even the scientific community at large, concerns itself with events in homogeneous media. However, chemical and physical processes at surfaces and interfaces are of fundamental importance in nature and in the technological society developed by humanity. Numerous examples of such events are available in medicine, biology, radiobiology, industry, etc., as well as in the new development of solar energy storage. A few choice examples, which follow, illustrate and stress the many important features of interfacial chemical events.

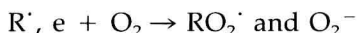
Biological Systems

A living cell is distinguished by possessing, among other things, a nucleus and a cell wall or membrane. The vital nature of the nucleus has been well impressed on the thinking of the community by many communications at all levels of sophistication. By contrast, the cell membrane or wall has received little notoriety and is often dismissed as a convenient "hold all" for the organism. Yet, through this structure the cell receives nutrients, eliminates waste products, and recognizes its environment. A failure in the cell membrane could be disastrous to the well-being of an organism. This lightly dismissed boundary contains the most sophisticated physicochemical apparatus that communicates information of vital importance to the cell. It may also participate in the decision-making faculty of the organism.

Medical science has realized the awesome consequences of "cell contact inhibition" (1). The outer membrane of a healthy cell contains molecules that recognize the situation where cells are in physical contact and cell multiplication has reached its limit. This information is interpreted by the cell as a signal to cease cell division. A damaged cell, one that is transformed virally or chemically, does not possess this critical faculty. Cell-to-cell contact is not recognized, and cell division proceeds ceaselessly leading to an altered life form or tumor. The damaged cell apparently has an alteration in the outer membrane that stops

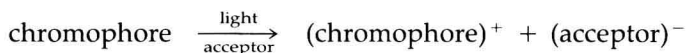
it from recognizing its surroundings accurately, and hence, leads to catastrophe.

The cell membrane also plays a crucial role in the treatment of cancer by high-energy radiation. In the early days of radiobiology oxic cells were found to be more sensitive to high-energy radiation than anoxic cells. Thus, increasing the oxygen content of tumor cells as much as possible is desirable so that lethal damage to the tumor is maximized. Oxygen is used up during the cell irradiation by chemical free radical species R^\cdot and ions e^- ,



The long-lived peroxy species RO_2^\cdot and O_2^- strongly promote damage to the cell. In a series of experiments with pulsed accelerators, high radiation doses decreased the cell oxygen level and maximum cell killing only occurred if sufficient time elapsed between radiation doses so that oxygen could penetrate through the cell membrane and into the cell (2, 3). The site of radiation damage in cells is the nucleus; however, the rather innocuous role of oxygen transport across the cell membranes plays a major part in the final result.

The role of a barrier given to a membrane is realized immediately in photosynthesis, where the primary step, the adsorption of a light quantum by the chloroplast chromophore, leads to electron transfer:



For this process to occur efficiently, the donor chromophore and acceptor must be arranged in close proximity so that efficient electron transfer occurs. A phospholipid membrane system is used to provide a matrix for the photosystems that are activated in the initial event. Even more important is the role played by the membrane in guaranteeing that back electron transfer, a process that would decrease the yield of the photoreaction, does not occur. The photoevents of vision are particularly complicated, because the information of the photons has to be communicated to the brain as electrical impulses passed along the nervous system. Numerous interfacial chemical processes take place along the nervous system, processes that are not well documented. However, the interfacial photon systems of the eye are still under vigorous investigation. The photosensory device of the eye is a rod or cone, which contains about 1000 closed bilayer membranes packed with rhodopsin molecules. Excitation of rhodopsin by absorption of light leads to isomerization of 11-*cis*-retinal to all-*trans*-retinal. This isomerization leads to a closing of the sodium ion channels in the plasma

membrane, which, in turn, lead to signals that are passed by the nervous system to the brain. Nature often uses an interface to achieve efficiency in a desired process. Those uses given in this section are pertinent to later considerations in this text.

Industrial Effects of Surfaces

Most articles in everyday use are covered by a layer of organic material. This layer serves both to protect the object from corrosion by the environment, and to provide a vehicle for color and for pleasant handling of the object. For the most part, an organic-based paint is used, and it provides a thin membranelike layer between the object and its environment. The analogy between the paint and the membrane ends there because the paint layer has little of the ordered and sophisticated properties of a membrane. However, diffusion of materials, in particular oxygen, through the paint layer and photolytic damage of the paint by light are reminiscent of similar effects in membranes.

The joining of two surfaces by an adhesive is an important industrial technique. The surfaces of the objects to be bonded together have to readily receive the adhesive, which in most cases is a foreign material. The subsequent setting or polymerization of the adhesive has to proceed smoothly, in spite of the solid structures into which it has diffused. The chemistry and physics of such processes are complex and are modified by the narrow object–adhesive interface. The diametrically opposite effect of lubrication also operates at a thin interface of object and lubricant.

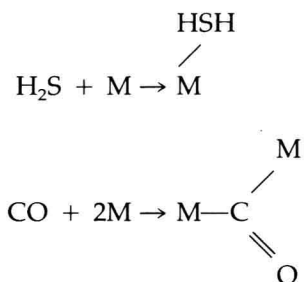
Catalysis

In the examples just discussed, the interface between two materials is important, mainly because of the specialized physical properties imparted to the system by the interface. Often, the chemistry at interfaces is altered or different from the norm, that is, from that experienced in homogeneous media. The unique properties of an interface are used in catalysis, and many outstanding solid-state catalysts that promote reactions of great value are available in industry. Catalysis is due to adsorption of the reactants on the catalyst surface. The nature of the adsorption may give rise to low levels of active species (4, 5). For example, H_2 probably is adsorbed on some surfaces as atoms:



where M denotes an active site on the catalyst. Other molecules may

be adsorbed at an active state without dissociation, for example, H_2S , or CO .



The adsorbed molecules are in a higher energy state than free molecules.

Reactions are catalyzed because the activation energy of the reaction is lowered. The reactants are also organized on the catalyst in a suitable form for reaction to occur, and are maintained in close proximity on the catalyst during the course of reaction. The rapid three-dimensional, rotational, and translational motion of free reactants is eliminated in favor of a more rigid situation where reactants are brought together slowly but for long periods of time. The relative importance of lowering the activation energy compared to optimum alignment of molecules is not known with industrial catalysts. This concept will be discussed further in the section on colloidal systems.

Photosystems

Photochemistry in heterogeneous systems is of particular importance in the photoimaging industry, where phototechniques are used in the production of literature and textiles and in the preparation of printed electronic circuits (5, 6). Most photographic imaging is carried out with silver-based systems. However, in the future efficient nonsilver systems would probably be based on heterogeneous emulsion systems. Many immediate difficulties are encountered in the development of such systems (7), but some colloidal surfactant systems show promise. Heterogeneous chemistry across two phases is an essential feature of all systems.

Solid-state solar devices, which convert solar energy to electrical energy, have become important because of the diminishing world stocks of oil. These systems consist of solid materials that eject electrons to a conductor when light impinges on them. The event is again photochemistry at an interface. Developments in this area have led to the design of low cost solar cells and the increase in their response to the solar spectrum (8, 9). Most of the systems considered to be possible

avenues for solar energy research (10) involve the use of membranes or colloids, that is, chemistry at interfaces.

Radiation as a Catalyst

Chemistry initiated by the absorption of radiation may be looked upon as a catalyzed reaction. In thermal catalysis the reactants are strained by the catalyst and become energized for efficient rapid reactions. Absorption of radiation also leads to energized molecules and promotes reaction. However, the energies involved can be much larger than those involved in thermal catalysis; usually, the action of radiation is to produce chemistry that does not occur thermally. This method is at odds with thermal catalysis where chemical reaction does occur slowly in the absence of the catalyst. The convenience of a radiation-induced reaction cannot be overemphasized, however, as efficient and unusual reaction is promoted readily without introducing a foreign body into the reactants. Radiation-induced processes depend rather critically on the nature of the medium in which they are carried out and tend to be difficult to control or marshall into desired reaction pathways. This area is where the value of a directing system comes into play, that is, the introduction of a catalyst that promotes one of the radiation-induced reactions at the expense of the others. Perhaps the term catalyst is a little misleading because the chemical reactions already occur as a result of the action of radiation absorption; just guidance is required. Interfaces introduced into the chemical systems via colloidal particles provide starting routes for the desired effect of control of the radiation-induced reaction.

Photochemistry and radiation chemistry have been carried out in solution and, to benefit from the large body of work already available, catalysts that can be used in fluid media must be studied. Colloidal chemistry provides many such systems from organic micelles to colloidal metals. For the most part, these systems consist of small particles (radii of 20–2000 Å) suspended in liquids such as water or hydrocarbons. Other systems may utilize other liquids, but little is known about them. The interface or surface exists between the particle and the bulk fluid medium. The nature of the interface (i.e., surface charge and surface type) may be changed readily to promote optimum conditions for reaction. These systems have provided useful vehicles for the catalysis of thermal reactions (11, 12), and can promote radiation-induced reactions (12–15). In many instances, the knowledge gained from studies of the radiation-induced reactions can be used to comment on the structure of the colloidal particle. It is useful to consider the colloidal particle as an *organized assembly* that organizes the reactions taking place at the particle.