

The Handbook of Environmental Chemistry

Volume 2 Part B

Reactions and Processes

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With Contributions by

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With 63 Figures



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Edited by O. Hutzinger

Preface

Environmental Chemistry is a relatively young science. Interest in this subject, however, is growing very rapidly and, although no agreement has been reached as yet about the exact content and limits of this interdisciplinary discipline, there appears to be increasing interest in seeing environmental topics which are based on chemistry embodied in this subject. One of the first objectives of Environmental Chemistry must be the study of the environment and of natural chemical processes which occur in the environment. A major purpose of this series on Environmental Chemistry, therefore, is to present a reasonably uniform view of various aspects of the chemistry of the environment and chemical reactions occurring in the environment.

The industrial activities of man have given a new dimension to Environmental Chemistry. We have now synthesized and described over five million chemical compounds and chemical industry produces about hundred and fifty million tons of synthetic chemicals annually. We ship billions of tons of oil per year and through mining operations and other, geophysical modifications, large quantities of inorganic and organic materials are released from their natural deposits. Cities and metropolitan areas of up to 15 million inhabitants produce large quantities of waste in relatively small and confined areas. Much of the chemical products and waste products of modern society are released into the environment either during production, storage, transport, use or ultimate disposal. These released materials participate in natural cycles and reactions and frequently lead to interference and disturbance of natural systems.

Environmental Chemistry is concerned with *reactions in the environment*. It is about distribution and equilibria between environmental compartments. It is about reactions, pathways, thermodynamics and kinetics. An important purpose of this Handbook is to aid understanding of the basic distribution and chemical reaction processes which occur in the environment.

Laws regulating toxic substances in various countries are designed to assess and control risk of chemicals to man and his environment. Science can contribute in two areas to this assessment; firstly in the area of toxicology and secondly in the area of chemical exposure. The available concentration ("environmental exposure concentration") depends on the fate of chemical compounds in the environment and thus their distribution and reaction behaviour in the environment. One very important contribution of Environmental Chemistry to the above mentioned toxic substances laws is to develop laboratory test

methods, or mathematical correlations and models that predict the environmental fate of new chemical compounds. The third purpose of this Handbook is to help in the basic understanding and development of such test methods and models.

The last explicit purpose of the Handbook is to present, in concise form, the most important properties relating to environmental chemistry and hazard assessment for the most important series of chemical compounds.

At the moment three volumes of the Handbook are planned. Volume 1 deals with the natural environment and the biogeochemical cycles therein, including some background information such as energetics and ecology. Volume 2 is concerned with reactions and processes in the environment and deals with physical factors such as transport and adsorption, and chemical, photochemical and biochemical reactions in the environment, as well as some aspects of pharmacokinetics and metabolism within organisms. Volume 3 deals with anthropogenic compounds, their chemical backgrounds, production methods and information about their use, their environmental behaviour, analytical methodology and some important aspects of their toxic effects. The material for volume 1, 2 and 3 was each more than could easily be fitted into a single volume, and for this reason, as well as for the purpose of rapid publication of available manuscripts, all three volumes were divided in the parts A and B. Publisher and editor hope to keep materials of the volumes one to three up to date and to extend coverage in the subject areas by publishing further parts in the future. Readers are encouraged to offer suggestions and advice as to future editions of "The Handbook of Environmental Chemistry".

Most chapters in the Handbook are written to a fairly advanced level and should be of interest to the graduate student and practising scientist. I also hope that the subject matter treated will be of interest to people outside chemistry and to scientists in industry as well as government and regulatory bodies. It would be very satisfying for me to see the books used as a basis for developing graduate courses on Environmental Chemistry.

Due to the breadth of the subject matter, it was not easy to edit this Handbook. Specialists had to be found in quite different areas of science who were willing to contribute a chapter within the prescribed schedule. It is with great satisfaction that I thank all 52 authors from 8 countries for their understanding and for devoting their time to this effort. Special thanks are due to Dr. F. Boschke of Springer for his advice and discussions throughout all stages of preparation of the Handbook. Mrs. A. Heinrich of Springer has significantly contributed to the technical development of the book through her conscientious and efficient work. Finally I like to thank my family, students and colleagues for being so patient with me during several critical phases of preparation for the Handbook, and to some colleagues and the secretaries for technical help.

I consider it a privilege to see my chosen subject grow. My interest in Environmental Chemistry dates back to my early college days in Vienna. I received significant impulses during my postdoctoral period at the University of California and my interest slowly developed during my time with the

National Research Council of Canada, before I could devote my full time to Environmental Chemistry, here in Amsterdam. I hope this Handbook may help deepen the interest of other scientists in this subject.

O. Hutzinger

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Basic Principles of Environmental Photochemistry

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Introduction

Environmental photochemistry may be considered as a sub-discipline within the field of photochemistry as it has been known for many decades. The distinction serves only to emphasize the specific conditions under which this type of photochemistry is carried out. Special fields of environmental photochemistry are atmospheric photochemistry, aquatic (marine) photochemistry, and photochemistry at surfaces and interfaces, subjects that received extensive coverage in this Handbook.

The basic fundamentals of photochemistry apply to all of these subjects. It is felt therefore that a brief introduction into the basic background of absorption processes and the various deactivation pathways for electronically excited molecules, of which chemical reactivity is the most important to the environmental chemist, would be in order. For a much more detailed discussion on the basics of photochemistry the reader should consult the appropriate textbooks [1-7].

In the second part of this introductory chapter an attempt was made to outline the special features of environmental photochemistry.

Basic Photochemical Processes

Definitions, Laws and Rules of Photochemistry

Photochemistry can be defined as the study of the chemical processes which occur after electronic excitation of molecules with electromagnetic radiation.

The laws and rules of photochemistry are:

1. Only the radiation absorbed by a molecule can be effective in producing a photochemical change in the molecule. (Grotthus-Draper).

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2. Each photon absorbed can activate only *one* molecule in the primary step of a photochemical sequence (Stark-Einstein).
3. Each photon absorbed has a certain probability of populating the lowest singlet and triplet excited states of a molecule.
4. Normally, only the lowest electronically excited states (singlet or triplet) are important for studying photochemical processes.

The second law is sometimes rephrased by the following: The absorption of radiation by a molecule is a one-quantum process, so that the sum of the primary process quantum yields must be unity ($\sum_i \phi_i = 1$).

The emphasis here is on the primary processes, as in gas-phase photo-chlorination ϕ_{HCl} can be as large as 10^5 – 10^6 by a radical chain process.

The quantum yield is a measure of the efficiency of photon usage and is represented by:

$$\phi = \frac{\text{number of molecules involved in a process}}{\text{total number of photons absorbed by the system}}$$

The concept of quantum yields can be used for both photochemical and photo-physical processes. In the former case it is just the ratio of the number of moles of product formed (or substrate disappeared) and the total number of Einsteins (= moles of photons) absorbed by the system.

Interaction of Radiation with Molecules: Absorption

Electromagnetic radiation, of which visible light and ultra-violet radiation are examples, can be envisaged in terms of an oscillating electric field and an oscillating magnetic field operating in planes which are perpendicular to each other and to the direction of propagation. For some purposes it is more convenient to use a particle description of electro-magnetic radiation, since radiation of a given frequency is quantized and is absorbed, emitted and transmitted in discrete units, photons, whose energy E is directly related to the frequency ν by:

$$E = h\nu,$$

where h is Planck's constant (6.62×10^{-27} erg.s./photon). When a photon passes close to a molecule there is an interaction between the electric field associated with the molecule and that associated with the radiation. Molecular excitation by absorption of radiation takes place during the period of one vibration of the exciting radiation wave. For radiation with a wavelength $\lambda = 300$ nm, this corresponds to 10^{-15} s; this time period is too short¹ for a change in geometry to occur. Hence the initially formed excited state must have the same geometry as the ground state molecule, which is referred to as the Franck-Condon principle. The energy associated with radiation of $\lambda = 300$ nm corresponds to about $403 \text{ kJ} \cdot \text{mole}^{-1}$ or $96 \text{ kcal} \cdot \text{mole}^{-1}$.

¹ A typical vibration of a carbonyl group with 1.6μ would correspond with a frequency of $5 \times 10^{13} \text{ s}^{-1}$ of the interacting radiation

The absorption of radiation by a homogeneous absorbing system is described by the familiar combined Beer-Lambert laws. It is a combination of the two empirical laws:

- Lambert's law: The fraction of radiation absorbed by a system is independent of the intensity of that radiation.
- Beer's law: The amount of radiation absorbed by the system is proportional to the number of molecules absorbing the radiation.

From these laws, the well-known Beer-Lambert equation is obtained:

$$I = I_0 \cdot 10^{-\varepsilon \cdot c \cdot l}$$

and:

$$E = \varepsilon \cdot c \cdot l = \log(I_0/I),$$

where E = Absorptivity (Optical density), I_0 = intensity before absorption, I = intensity after absorption, ε = molar extinction coefficient, c = concentration of the absorbing system, and l = (optical) pathlength.

With the introduction of the concept of transmission ($T = I/I_0$) the absorptivity equals:

$$E = -\log T.$$

For these relations to hold rigorously, interactions between the molecules must be unimportant at all concentrations. Deviations occur in the case of molecular associations, or dimerizations (which are usually not very likely with 'environmental' concentrations). The law is also invalid when very high intensities of radiation are employed (e.g. when using lasers) and a significant proportion of the molecules in a given region are in the excited state rather than in the ground state at any one time. With highly fluorescent compounds, a false measure of the transmitted beam intensity may be received by the detector and lead to an apparent failure of the basic absorption law. When more than one absorbing compound is present in a homogeneous mixture, the Beer-Lambert equation assumes the form:

$$I = I_0 \cdot 10^{-(\varepsilon_1 c_1 + \varepsilon_2 c_2 + \varepsilon_3 c_3 + \dots)l},$$

where ε_1 and c_1 refer to compound 1, ε_2 and c_2 to compound 2 etc. at a particular wavelength.

If the incident intensity is known, the absorbed intensity I_a can be calculated, since:

$$I_a = I_0 - I_t$$

and thus from Beer's law:

$$I_a = I_0 (1 - e^{-2.3 \varepsilon \cdot c \cdot l}).$$

Two conditions make the use of this equation easier:

1. If all incident light is absorbed ($E > 2$), then $I_a = I_0$;
2. If very little of the light is absorbed ($E \leq 0.05$), then

$$I_a \sim 2.3 \varepsilon \cdot c \cdot l \cdot I_0.$$

An alternative measure of absorption intensity, which can be related more readily to theoretical principles is the oscillator strength, f , given by the equation:

$$f = 4.315 \times 10^{-9} \int \epsilon dv.$$

The major difference between oscillator strength and extinction coefficient is that the former is a measure of the integrated intensity of absorption over a whole band, where ϵ is a measure of the intensity of absorption for a single wavelength.

The absorption of radiation is associated with an electronic transition of the molecule (excited state). The probability of occurrence of such a transition and hence the intensity of the associated absorption band is dependent upon various factors. These factors are included in selection rules which govern whether a transition will be allowed or forbidden. Transitions which conform to the selection rules can give rise to very intense absorption bands, i.e. bands with high f and high ϵ_{\max} values. Transitions which do not conform to the selection rules either do not occur or else the probability of occurrence is so low that only very weak bands are observed in the spectrum.

The selection rules for polyatomic molecules can be represented in relation to the oscillator strength f_a of a fully allowed $\pi-\pi^*$ transition by the equation:

$$f = p_s \cdot p_o \cdot p_p \cdot p_m \cdot f_a,$$

where f is the oscillator strength for the transition under consideration and the terms p_s , p_o , p_p , and p_m are probability factors which respectively take into account the changes in electron spin, orbital symmetry, parity and momentum, which occur as a result of the electronic transition.

For a discussion on these probability factors, the reader is referred to the textbooks.

Photophysical and Photochemical Processes

Non-Radiative Deactivation

In Fig. 1 a simplified Jablonski diagram is shown. This indicates the routes of deactivation for a molecule after excitation. Some routes are radiationless (wavy arrows), others do emit a quantum of radiation (generally of lower energy than the exciting wavelength) denoted by straight arrows.

A closer look at the Jablonski (state) diagram reveals that each electronic state has also vibrational levels which are in general of no importance for photochemical processes, as the relaxation from higher vibrational levels within each electronic state (called vibrational relaxation or vibrational cascade) is very fast (of the order of 10^{12} s^{-1}). A somewhat slower, but still appreciably fast process is the decay of one electronic state to a lower state of the same multiplicity. This process, called internal conversion, can be considered to be the "fitting" of some vibrational level of e.g. S_2 (denoted by S_i) with a vibrational level of e.g. S_1 (denoted by S_j) which may not have exactly the same energy, but can be made so by thermal equilibration. The (internal) conversion from S_i to S_j should be an iso-energetic process, that is followed by vibrational relaxation of the new vibrationally "hot" state. The internal conversion process is fast and has a range between 10^{12} and 10^6 s^{-1} .