REACTION MECHANISMS IN ENVIRONMENTAL ORGANIC CHEMISTRY

Richard A. Larson
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LEWIS PUBLISHERS

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RAL:

To the memory of James Wright
1928–1980

Poet, educator, sage

Morir com'esso, ma morir segundo te.

EJW:

To my wife, Jodi, and children, Joel and Sarah, for their love, support and patience during the writing of this book, and to my chemistry mentors, Dr. Christopher J. Dalton at Bowling Green State University and Dr. Scott E. Denmark at the University of Illinois, who provided me with a fundamental education in organic chemistry.

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Richard A. Larson (BA, Chemistry, University of Minnesota, 1963: PhD, Organic Chemistry, University of Illinois, 1968) has had extensive research experience over the past 20+ years in the area of environmental chemistry. He has been author or coauthor of well over 100 papers, presentations, and reports in this period, including over 70 peer-reviewed manuscripts. In addition, he is the author, coauthor, or editor of three books.

After postdoctoral appointments at Cambridge University and the University of Texas, Dr. Larson worked for several years at the Academy of Natural Sciences of Philadelphia. Since 1979, when he joined the faculty of the Institute for Environmental Studies at the University of Illinois, Dr. Larson has held a joint appointment in the University's Department of Civil Engineering. During the academic year 1985–1986, he studied free radical reactions in water as a National Research Council senior fellow in collaboration with Dr. Richard Zepp at the U.S. Environmental Protection Agency research laboratory in Athens, Georgia.

Dr. Larson has worked principally in the specific research areas of environmental photochemistry (kinetics, mechanisms, and products of light-induced reactions of environmental significance), disinfectant chemistry (ozone, chlorine, and chlorine dioxide and their reactions with organic compounds), and natural product chemistry. He is especially interested in the reactions of polar organic compounds of potential environmental health significance.

Eric J. Weber (BS, Chemistry, Bowling Green State University, 1980; PhD, Organic Chemistry, University of Illinois, 1985) received his initial training in synthetic and physical organic chemistry. During his PhD program he developed an interest in environmental chemistry after taking a course from his current co-author, Dr. Richard Larson, focusing on the fate of organic chemicals in aquatic ecosystems. Upon completion of his PhD, Dr. Weber furthered his training in environmental chemistry as a Research Associate with the National Research Council at the U.S. Environmental Protection Agency research laboratory in Athens, Georgia. In 1986, he joined the staff at the Athens laboratory as a Research Chemist. Dr. Weber's research has focused on transformation pathways of organic chemicals at the sediment-water interface with a primary emphasis on the identification of reaction products. He has also developed an interest in elucidating the reaction mechanisms by which organic chemicals form covalent bonds with natural organic matter.

PREFACE

Environmental organic chemistry is a rapidly expanding subject and one that allows many perspectives. Environmental chemistry historically grew out of analytical chemistry and the ability of analytical chemists to detect very low concentrations of pollutants, especially chlorinated organic compounds, in complex matrices such as soils, atmospheric particles, and animal tissues. The discovery that such pollutants are transported throughout the world, and that some are highly persistent in the environment, led to increasing interest in the fates of such compounds in nature.

The physical and chemical factors that govern the transport of organic compounds in the environment have been intensely studied. Thanks to the work of Sam Karickhoff, Donald Mackay, Cary Chiou, Louis Thibodeaux, and many others, we now have a group of sophisticated modeling tools with which to investigate the movement of organic materials within and between various environmental compartments—air, water, soils and sediments, and biota. Organic reactions that transform particular chemicals into by-products, however, have received less attention. There are several reasons for this. First of all, most investigations of organic chemical reactions have been performed in the absence of water. Rigorous procedures for the exclusion of moisture, and often, oxygen from reaction mixtures are commonplace in the organic laboratory. Secondly, organic reactions can be extremely complex. Even in purified solvents using carefully controlled conditions, many products can be formed whose identification may tax the ingenuity of the investigator. Finally, in many environmental situations, readily identified organic compounds are present only in extremely small concentrations in the presence of a complex matrix. In order to study the fate of pollutants under these conditions, early practitioners of environmental organic chemistry found it difficult enough merely to determine the rates of disappearance of their substrates, let alone to determine the mechanisms and products of the reactions that they were undergoing.

Recent years have seen an expansion of interest in studying organic reactions under environmental conditions. Many studies have shown that the environmental alteration products of some organic molecules are much more hazardous than their precursors; for example, treatment of natural waters with chlorine causes potentially

toxic or mutagenic organochlorine compounds to be formed. Moreover, a general curiosity about how the global environment functions has led to a desire for intellectual re-examinations of fundamental scientific issues, such as the carbon cycle and the effects of human activities on it. To acquire this fundamental knowledge, it is necessary that we understand the forces that drive these global processes. As a consequence, many scientists throughout the world are turning their attention to investigating some well-known chemical reactions in detail, with an eye to being able to use the knowledge gained to predict the fates of unknown synthetic chemicals that may be released in significant concentrations in the future.

It is the purpose of this book to assist this process by giving an overview of the environment, of the principal organic chemical species in it, and of the processes and reactions that tend to transform these species. The organization of the book features, first, an introductory chapter that lays out the three principal environmental compartments—air, water, and solid phases—and surveys the conditions found in each of them that tend to promote chemical reactions. The remainder of the book is a survey of the principal types of organic reactions that may occur under environmental conditions, with discussions of the particular structural features of organic molecules that may make them more or less susceptible to each type of reaction. Chapter 2 deals with hydrolyses and nucleophilic reactions, with many examples chosen from the literatures of pesticide chemistry, industrial chemistry, and physical organic chemistry. Chapter 3 covers reduction, a process that until recently has been neglected from an environmental perspective, but one that is being shown to be an increasingly important route for converting many compounds once thought to be “persistent” to products. Oxidation, the subject of Chapter 4, takes place in a range of environments from the upper atmosphere to the surfaces of sediments, and encompasses a plethora of oxidizing agents, from transient free radicals with lifetimes of microseconds to mundane minerals such as iron oxide. In Chapter 5, disinfection is addressed; these reactions and their projects are the subjects of public debate in virtually every community where water treatment is practiced. Sunlight-induced reactions are covered in Chapter 6, on photochemistry. These reactions are also sure to come under increasing scrutiny, as the world tries to adjust to life under a different regime of solar energy, featuring higher levels of short, energetic UV-B wavelengths. Finally, Chapter 7 introduces a few other reactions that do not fit under the previous categories, but nevertheless could be significant for the fates of many classes of compounds.

The production of this book has been the outcome of many hours of discussions over the years. The two coauthors have learned a great deal from each other as well as from our many colleagues, students, and friends. An incomplete list of the most important people to whom we owe debts of gratitude would include Mike Barcelona, Michael Elovitz, Bruce Faust, Chad Jafvert, Karen Marley, Gary Peyton, Frank Scully, Alan Stone, Paul Tratnyek, Lee Wolfe, Ollie Zafirio, and Richard Zepp. Invaluable help with the manuscript was provided by Jean Clarke, Tori Corkery, Jennifer Nevius, and Heather Walsh. Finally, special thanks are due to the students of Environmental Studies 351 at the University of Illinois, who have provided indispensable suggestions about the subject matter of this book over the years.

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If the Lord Almighty had consulted me before embarking upon the Creation, I should have recommended something simpler.

—*ALPHONSO X OF CASTILE ("THE WISE")*

Strange events permit themselves the luxury of occurring.

—*"CHARLIE CHAN" (CREATED BY EARL DERR BIGGERS)*

The map appears to us more real than the land.

—*D. H. LAWRENCE*

Organic chemistry just now is enough to drive one mad. It gives the impression of a primeval, tropical forest full of the most remarkable things, a monstrous and boundless thicket, with no way of escape, into which one may well dread to enter.

—*FRIEDRICH WÖHLER (1845)*

There is something fascinating about science. One gets such wholesale return of conjecture out of such a trifling investment of fact.

—*MARK TWAIN*

Reality may avoid the obligation to be interesting, but hypotheses may not.

—*JORGE LUIS BORGES*

God loves the noise as much as the signal.

—*L. M. BRANSCOMB*

This world, after all our science and sciences, is still a miracle.

—*THOMAS CARLYLE*

CHAPTER 1

ORGANIC CHEMICALS IN THE ENVIRONMENT

A. ENVIRONMENTAL FATES OF ORGANIC CHEMICALS

This book will mainly be about **environmental fate processes**, and in particular about a certain subset of these fate processes; namely, organic chemical reactions. Specifically, if a particular organic chemical is introduced into the environment, what will happen to it? How much can we tell from physical measurements of the chemical's properties, how much can we learn from lab experimentation, and how much do we need to learn directly from measurements on the chemical in the actual environment? The sort of questions that have been asked are:

1. Where does it go?
2. How long will it remain?
3. What are the products of its reactions?

We need this information for two reasons: the first is **intellectual**; that is, the knowledge we gain from such studies helps us to explain the functioning of the natural world and the cycling of naturally occurring materials; secondly, from a **practical** standpoint, we need the information for large-volume synthetic organic chemicals in order to predict their effects on human health and on ecosystem functioning. In principle, it should be possible to use chemical concepts derived from studies of the natural environment to forecast the fates of chemicals in the human,

or engineered, environment; or, possibly, the flow of information could proceed in the opposite direction.

Philosophically, environmental organic chemists make use of traditional reductionist assumptions and arguments. An organic compound, when discharged into a milieu that manifests a given array of chemical and physical conditions, should, it is believed, respond in a predictable manner to the constraints of those conditions. Although these responses may depend on an apparently bewildering assortment of chemical, physical, and biological qualifications, given sufficient information the fate of the compound should be predictable.

The subject matter of this book is an attempt to classify and organize what is known about the reactions of environmentally important organic compounds, using concepts and data largely drawn from traditional mechanistic and physical organic chemistry. We hope this approach will help the reader understand these reactions and their importance for the environmental fates of organic compounds of many types. The book has a molecular and mechanistic emphasis. We will take particular organic molecules and look at their fates in an aquatic ecosystem context. We will discuss their reactions in terms that an organic chemist would use. However, we will need to bring in concepts from biology, ecology, geochemistry, and environmental engineering. The purpose of this introductory section is to give background data to assist the reader's understanding of organic chemicals and their fates under environmental conditions.

1. The Carbon Cycle

In order to begin a consideration of the fate of organic compounds in nature, it is worthwhile to take a look at the carbon cycle. The discussion of the carbon cycle which follows is largely drawn from Woodwell and Pecan (1973), Bolin (1979) and Bolin and Cook (1983). A diagram of the carbon cycle (Figure 1.1) is intended to show the interconversions and movements of carbonaceous species, both organic and inorganic, throughout the earth's gaseous, liquid, and solid phases, as well as processes mediated by living organisms. Inorganic compounds are located principally on the left and top sides of the diagram, and organic matter is localized in the lower right portions. The boundary between inorganic and organic carbon species is rather arbitrary; metal carbides and cyanides intuitively seem to be inorganic compounds, but salts of organic acids do not. Carbon disulfide, $S=C=S$, is normally considered an "organic solvent," yet carbonyl sulfide, $O=C=S$, has an inorganic quality. Regardless of these borderline cases, in geochemical terms inorganic carbon is overwhelmingly dominated by carbon oxides and carbonates. Similarly, compounds of carbon containing covalent bonds to C, H, O, N, S, P, and halogens constitute the vast majority of organic compounds in the carbon cycle.

Fundamentally, the carbon cycle is a series of linked chemical reactions, both biological and abiotic. Many are redox reactions. Although the principal source of energy that drives the global redox system is sunlight, humans have not only diverted naturally occurring sources of energy and carbon to their own use, but are also

Figure 1.1. Diagram of the carbon cycle, showing movement of oxidized and reduced carbon species between the atmosphere, hydrosphere, biosphere, and geosphere.

contributing ever-increasing amounts of energy (and volatile carbon) to the system by virtue of fuel-burning and managed agriculture. In the Northern Hemisphere, anthropogenically generated energy now exceeds biotic energy flux (photosynthesis). This phenomenon has been called the “civilization engine” (Stumm and Morgan, 1981).

The carbon cycle is not complete—there are some sinks or areas where compounds accumulate, or are at least very slowly turned over. The approximate masses of carbon in the various atmospheric and terrestrial carbon pools and some of their approximate annual rates of conversion are given in Table 1.1.

The most oxidized species, CO_2 , exists in the atmosphere as a gas whose concentration far exceeds that of other carbon-containing substances. In water, it takes part in a series of equilibrium reactions involving hydration, ionization, and precipitation:

Table 1.1. Some Components of the Carbon Cycle (Estimated magnitudes in grams of C)

Reservoirs		Annual Transport Rates	
<i>Atmospheric</i>		Atmosphere to oceans	1×10^{17}
CO ₂	7.3×10^{17}	Land to oceans	
CO	2.27×10^{14}	Inorganic C	4×10^{14}
CH ₄	3×10^{15}	Dissolved org. C	1×10^{14}
Nonmethane organic C	5×10^{13}	Particulate org. C	6×10^{13}
Freons	1×10^{11}	Net land primary production	6×10^{16}
<i>Aquatic</i>		Net oceanic primary production	6×10^{16}
Inorganic C	1×10^{20}	Animal respiration	8×10^{16}
Dissolved organic C		Microbial respiration	4×10^{16}
0–200 m	9×10^{16}	Plant litter production	5×10^{16}
> 200 m	9×10^{17}	Algal excretion	4×10^{16}
Particulate organic C	3×10^{16}	Human harvest (cereals)	6×10^{14}
Plankton	3×10^{15}	Human harvest (wood products)	5×10^{14}
Bacteria	2×10^{14}	Fossil fuel combustion	5×10^{15}
<i>Terrestrial</i>		Synthetic organic chemical production	1×10^{14}
Rocks and sediments	2×10^{22}		
Coal, oil and peat	7×10^{18}		
Soil humic material	2×10^{18}		
Organisms (total)	7×10^{17}		
Living phytomass	5.6×10^{17}		
Dead phytomass, litter	9×10^{16}		
“Wild animals”	3×10^{15}		
Livestock	1.2×10^{14}		
Humans	2.4×10^{13}		
Bacteria, fungi	5×10^{15}		

Sources: Woodwell and Pecan (1973), Bolin (1979), and Bolin and Cook (1983).

that transport it throughout the aqueous and solid phases. Carbon dioxide gas dissolves in water to form carbonic acid, a weak acid. Therefore, pure water containing CO₂ becomes slightly acidic; the pH of rain water at equilibrium with CO₂ is 5.5. (Obviously, atmospheric water containing dissolved nitrogen or sulfur oxides will be much more acidic.) The first proton of carbonic acid ionizes to the monovalent anion, bicarbonate, with a pK_a of 6.4. Thus at equilibrium at pH 6.4, the concentrations of carbonic acid and bicarbonate will be equal. The second ionization to the divalent anion, carbonate, occurs with a pK_a of 10.4. However, in water

containing calcium ions or other ions that form insoluble carbonates, carbonate anion will rapidly be removed. Calcium carbonate exists in several forms, including limestone.

The photosynthetic activities of plants and, especially, algae that live in water remove some CO_2 from the water directly, and also increase the pH to such an extent that more carbonate occurs and precipitates out. The "shorthand" equation for photosynthesis explains the direct loss of CO_2 :

This formation of reduced carbon species and the simultaneous release of oxygen from carbon dioxide by plants is called "primary production" in ecological jargon.

A more accurate equation for photosynthesis (Stumm and Morgan, 1981) also explains the pH increase in natural waters containing photosynthesizing organisms:

The complex expression on the right-hand side of the equation is the average composition of algae. It can be seen that the process of photosynthesis results in a net consumption of hydrogen ions, and thus an increase in pH.

There are mechanisms for reconvertng CaCO_3 to soluble forms. One is simply to redissolve it using acid, such as acidic precipitation. A second way is to convert it back to bicarbonate using CO_2 :

The reverse of this reaction also occurs, for example when bicarbonate-containing water evaporates.

Looking at atmospheric CO_2 and its cycling, there is a total of 2.3×10^{18} grams of CO_2 in the atmosphere. Since the atmosphere weighs about 6.7×10^{21} g, this works out to 0.034% or 340 ppm. This has been increasing at about 1–2 ppm per year since at least 1957 (direct measurement), and probably well before. Samples of trapped air from the preindustrial period show concentrations between 260 and 295 ppm.

Concentrations of CO_2 are highest in the Northern Hemisphere in winter and drop sharply during the spring and summer. This is consistent with the increase being due to fossil fuel combustion. Estimates of the magnitude of present combustion-produced CO_2 are about 5×10^{15} g of C, (about 3 ppm of atmospheric CO_2) over and above natural CO_2 production by respiration, which is about 1.2×10^{17} g C/yr. Estimates of the cycling of naturally produced CO_2 are that 14% (1×10^{17} g C/yr) enter the oceans and 16% (1.2×10^{17} g) is taken up by photosynthetic organisms. Therefore, almost all of the atmospheric CO_2 is cycled in a three-year period. The extra carbon from combustion clearly does not all stay in the atmosphere; otherwise the observed increase would be 3 ppm/yr rather than 1–2 ppm/yr. It is still not certain whether the majority of the "missing" CO_2 dissolves in the ocean or is taken

up by plants. The increased CO_2 concentration probably, however, will not translate directly into increased biomass of plants around the world, because CO_2 is not usually the limiting substrate for plant growth; most ecologists believe that water and trace mineral nutrients are usually more important.

The respiration (metabolism) of the reduced carbon produced by plants returns it to the atmosphere as CO_2 . It is assumed that photosynthetic fixation of CO_2 from the atmosphere by plants and its return by respiration are in exact balance, but there is really no good way of telling. All that we know is that atmospheric carbon is increasing. An increase in CO_2 may affect the earth's surface temperature because the sun emits not only light (visible radiation energy), but also ultraviolet (UV) and infrared (IR or heat) radiation (see Section 6.A). When, for example, visible energy strikes the earth's surface, it loses energy and is partly converted to the lower-energy heat (IR) radiation, some of which is reflected back into space. Carbon dioxide is transparent to visible energy, but it strongly absorbs IR, so some of the heat generated near the earth's surface doesn't escape into the atmosphere. The net result is that the lower atmosphere becomes warmer.

A consideration of terrestrial carbon shows that inorganic carbon (carbonate rocks, mostly) predominates to a tremendous degree over organic carbon. There are very large reserves of "dead" organic carbon (coal, oil, peat, and soil humus), all ultimately derived from animals and plants which have died. Dead carbon (about 10^{19} g) exceeds living carbon by about 14:1. These materials, taken as an aggregate, are not rapidly recycled at the present rates of human utilization, although readily useful fossil fuels are exploited on a large scale.

Living carbon is largely (more than 80%) in higher plants. Most of this "phyto-mass" is in trees. About 30% of the land area of the earth is forested, but this proportion is decreasing. Tropical forests, which still constitute about 1/3 of the total forest area, are rapidly being cut down as the increasing population in developing countries exerts its requirement for living space and fuel.

The mass of the five billion or so living humans, about 240 billion kilograms, is only a few hundredths of a per cent of the total living biomass. Mankind's domestic livestock herds outweigh us by a factor of about 5, and all the "wild creatures," including all birds, mammals, lizards, fish, etc., by only about 20:1. The biomass of microorganisms, although difficult to estimate precisely, probably amounts to only a few per cent of all the living carbon.

Annually, we harvest about 10^{15} g, or about 50 times our own weight, in plant products including wood, fiber, and food. About 10% of the earth's land area is now being used for agriculture (including forestry). Other, urban, human institutions (housing, roads, industrial plants) consume between 1% and 2% of the surface of the globe (it has been estimated that 1% of the United States is paved). Densely populated countries have much more of their land area in urban use; for example, the Netherlands has about 9%. Synthetic organic chemical production has increased dramatically over the last 50 years, and now about 4×10^{14} g of such chemicals are produced annually (an amount close to the annual use of wood products).

To summarize, although the absolute effect of humans on the global quantity and flux of carbon has perhaps been modest, our contribution to changing the pattern of

the cycle has increased significantly in the last century or so. Given the serious lack of knowledge of the feedback mechanisms that tie various elements of the carbon system together, it would appear to be an urgent priority that we increase our understanding of the effects of our activities on these important planetary operations.

2. Translocation of Organic Chemicals

The fates of organic molecules (whether naturally or anthropogenically produced) include, first, **translocation**, in which the molecular structure of the chemical is not changed; a molecule will be carried between air, surface water, groundwater, organisms, aquatic sediments, and soils by various processes. Rates and equilibria can ideally be obtained to describe these transport processes, often by chemical engineering concepts like mass transfer equations, and to predict their extent. A good summary of environmental transport processes is given by Thibodeaux (1979).

Volatilization

Transport of organic compounds from the solid or aquatic phases to the gas phase (and back again) is now known to be a highly important process for the dispersion of chemical compounds around the globe. Dissolution into and volatilization from the aqueous phase is an elaborate process that depends on solubility, vapor pressure, turbulence within the two phases, and other physical and chemical factors. Volatilization of materials from the earth's surface into the troposphere can result in their long-range transport and redeposition, with the outcome being that measurable quantities of such substances can be detected far from their point of release.

Many chemicals escape quite rapidly from the aqueous phase, with half-lives on the order of minutes to hours, whereas others may remain for such long periods that other chemical and physical mechanisms govern their ultimate fates. The factors that affect the rate of volatilization of a chemical from aqueous solution (or its uptake from the gas phase by water) are complex, including the concentration of the compound and its profile with depth, Henry's law constant and diffusion coefficient for the compound, mass transport coefficients for the chemical both in air and water, wind speed, turbulence of the water body, the presence of modifying substrates such as adsorbents in the solution, and the temperature of the water. Many of these data can be estimated by laboratory measurements (Thomas, 1990), but extrapolation to a natural situation is often less than fully successful. Equations for computing rate constants for volatilization have been developed by Liss and Slater (1974) and Mackay and Leinonen (1975), whereas the effects of natural and forced aeration on the volatilization of chemicals from ponds, lakes, and streams have been discussed by Thibodeaux (1979).

Once a chemical becomes airborne, atmospheric mixing processes on regional, elevational, and global scales come into play. East-west mixing of air masses is much more efficient than north-south mixing. Because of the intra-hemispheric con-

straints on the prevailing winds, air masses seldom mix efficiently across the equator. The atmosphere becomes completely mixed only over very long time scales; for organic compounds with lifetimes of even several years, Northern and Southern Hemisphere variations are measurable if (as is usually the case) one hemispheric source predominates. Compounds of industrial origin are usually localized in the Northern Hemisphere, whereas substances derived from marine processes are usually more abundant in the Southern Hemisphere.

We know from studies of gases in solution that the solubility of a gas which does not react with its solvent depends to a considerable degree on its vapor pressure at a given temperature. We can extend these studies to other solutes if we can measure their vapor pressures at higher temperatures and extrapolate them to lower, environmentally realistic temperatures. For the case of air-water partitioning, a simple equation describes the behavior of many substances:

$$H = P/C \quad (1.5)$$

where **H** is the Henry's law coefficient for the chemical, **P** its vapor pressure, and **C** its water solubility. If we know or can estimate the quantities on the right-hand side of the equation, we can obtain **H**, and this will allow us to estimate the magnitude of the air-water partition.

Henry's law constants for chemicals of environmental interest have been tabulated by many authors, including Mackay and Shiu (1981), Burkhard et al. (1985), Gossett (1987), Murphy et al. (1987), Hawker (1989), and Brunner et al. (1990). If **H** has a relatively large value for a particular compound, it means that it has a large tendency to escape from the water phase and enter the atmosphere. To get a large value for **H**, obviously either a high **P** or a low **C** (or both) is required. Thus, for example, *sec*-butyl alcohol and decane have vapor pressures that differ by a factor of 10, with the alcohol being the higher, but because the hydrocarbon's water solubility is negligible, it is much more likely to enter the gas phase than is the alcohol. Similarly, although the pesticide DDT is essentially nonvolatile, its water solubility is far less even than decane's. As a result, a small quantity will be volatilized; this accounts for the widespread detection of DDT in environments far from the sites where it was applied. Another heavily applied chemical, the herbicide atrazine, is a little more volatile than DDT, but it is far more soluble, so its tendency to enter the atmosphere is negligible.

The movement of a chemical substance within the vapor phase occurs by the combined driving forces of flow and diffusion. An illustration of these effects can be visualized by considering a smokestack plume; in the absence of wind, the plume will rise vertically in a more or less uniform column until it reaches an elevation where density considerations result in its spreading out into a relatively broad and flat mantle. When wind is factored into the equation, the plume may move in a more nearly horizontal direction, more or less parallel to the surface of the ground, and at certain wind speeds the plume structure can break up into loops or bends due to turbulent aerodynamic effects such as eddy formation. In addition, small eddies can result in the breakdown of the coherent plume structure, with the formation of

vertical or horizontal regions of increasingly large cross-section and lower concentrations of plume constituents.

Transport Within the Aqueous Phase

The three-dimensional dispersion of a completely soluble organic solute within a volume of pure water will be governed by its rates of diffusion within the water column and by the flow characteristics of the water itself (also called *convection* or *advection*). In actual water bodies, complicating factors include the presence of particles of various sizes within the aqueous phase and the effects of boundary layers such as those associated with the air-water and sediment-water interfaces. Further complications occur in soil-water and groundwater systems in which the aqueous phase is a minor component in the presence of an excess of solid material (Thibodeaux, 1979).

Movement of a soluble chemical throughout a water body such as a lake or river is governed by thermal, gravitational, or wind-induced convection currents that set up laminar, or nearly frictionless, flows, and also by turbulent effects caused by inhomogeneities at the boundaries of the aqueous phase. In a river, for example, convective flows transport solutes in a nearly uniform, constant-velocity manner near the center of the stream due to the mass motion of the current, but the friction between the water and the bottom also sets up eddies that move parcels of water about in more randomized and less precisely describable patterns where the instantaneous velocity of the fluid fluctuates rapidly over a relatively short spatial distance. The dissolved constituents of the water parcel move with them in a process called eddy diffusion, or eddy dispersion. Horizontal eddy diffusion is often many times faster than vertical diffusion, so that chemicals spread sideways from a point of discharge much faster than perpendicular to it (Thomas, 1990). In a temperature- and density-stratified water body such as a lake or the ocean, movement of water parcels and their associated solutes will be restricted by currents confined to the stratified layers, and rates of exchange of materials between the layers will be slow.

The other method of diffusion of a chemical through a liquid phase, molecular diffusion, is driven by concentration gradients. It is normally orders of magnitude slower in natural waters than eddy-driven processes, unless the water body is abnormally still and uniform in temperature (Lerman, 1971). Such situations are found only in isolated settings such as groundwaters and sediment interstitial waters. Even here, however, empirical measurements often indicate that actual dispersion exceeds that calculated from molecular diffusion alone.

The transport of a substance through a water body to an interface may involve eddy or molecular diffusion through aqueous sectors of differing temperature, such as those characteristic of stratified lakes (cf. Section 1.B.2c), and through interfacial films such as air-water surface layers (Thomas, 1990). Conditions near a phase boundary are very difficult to model accurately. The resistance to diffusion through various regions may vary by large amounts, and the overall transfer rate is governed by the slowest step, which usually occurs in a thin film or boundary layer near the

interface where concentration gradients are large and molecular diffusion becomes influential.

Transport of a dissolved substance through a porous medium like a sandy soil, in which interaction between the solute and the solid phase is negligible, is governed by laws of mass transport that are similar to those that apply in solutions. When interactions with a solid phase such as a soil become significant, a situation similar to solid-liquid chromatography develops; solutes with less interaction with the "support," or soil, are moved along with the "solvent front" of water leaching through the medium, whereas others are held back in proportion to their degree of binding. Studies of this phenomenon in artificial microcosms such as soil columns or thin-layer chromatography plates are useful in helping to predict which compounds are likely to contaminate groundwater (see Section 1.B.2e). The predictions can be tested in field studies using wells or lysimeters.

Partition into Solid Phases

The transfer of molecules from solution into an environmental solid phase such as a soil or sediment is referred to as sorption, with the reverse process usually called desorption (Karickhoff, 1984; Weber et al., 1991). A variety of solid phases are available in the aquatic environment: small suspended particles, both living and nonliving, the anatomical surfaces of larger biota such as fish, and bulk soils and bottom sediments. Even colloidal organic "solutes" such as humic macromolecules might be thought of as separate phases to which a dissolved molecule could be sorbed. Each of these surfaces may be thought of as a source or a sink for compounds in solution.

The passage of a compound from solution into a solid environment can be promoted or inhibited by a variety of factors. Sorption and desorption equilibria are, for example, strongly temperature-dependent. In addition, the surface area of the solid, as well as its physicochemical characteristics (charge distribution and density, hydrophobicity, particle size and void volume, water content) are major factors that determine the importance and extent of sorption for a particular solute. In thermodynamic terms, for sorption to occur, the energy barrier associated with bringing the interacting species into proximity must be overcome by a greater decrease in free energy in the sorbed system. By measuring the heat of adsorption, some insight can be gained as to whether the sorption process is primarily due to physical (van der Waals-type) uptake or to chemical reaction, with physical uptake usually involving much lower (< 50 kJ/mol) energy differentials than chemical reactions, which have heats of adsorption in the range of 150 to 400 kJ/mol.

Although distinctions are sometimes made between adsorption (uptake of compounds by the surface of a solid phase) and absorption (diffusion of molecules into the interior of a solid), it is usually not possible to distinguish between these cases in environmental situations. A complicating factor in sorption studies is that natural solid phases are not only not chemically and physically homogeneous, but are normally coated with extraneous materials such as transition metal oxides, microor-

ganisms and their excretion products, and humic substances that often almost completely disguise the sorption properties of the underlying mineral.

Sorption is important from the viewpoint of chemical reactivity, as well. A compound that is sorbed usually goes from a situation in which it is entirely surrounded by water molecules to one in which it is in a mineral environment rich in organic matter. In fact, a chemical substance in a suspension of natural particulate matter will exist in a complex equilibrium in which a fraction of the material is dispersed into several disparate phases that may contribute differently to the reactions the substance may undergo.

Studies of the uptake of organic compounds by many types of natural solid phases (soils and sediments) in the presence of water have clearly shown that only two types of interactions are important: first, a coulombic interaction, in which organic compounds of opposite (positive) charge are sometimes taken up by the (usually) negatively charged solid material; and, generally more important, a hydrophobic interaction in which nonpolar organic compounds are attracted into the solid phase.

Among the most important constituents of most natural soils and sediments are the clay minerals (see Section 1.B.3a). These minerals usually exist as very fine ($< 1 \mu\text{M}$) particles with high surface area and (usually) negative charge. This makes them potent adsorbents for cations, either inorganic or organic, and leads to the possibility of cation-exchange displacement reactions. There may also be important pH effects at clay surfaces, especially in soft waters where cations other than H^+ are not abundant. It has been found that the pH near the surface of certain types of clay may be as much as 2 units lower ($[\text{H}^+]$ 100-fold higher) than in the associated solution (McLaren, 1957; see Section 1.B.3a). Obviously, there may be significant effects on the rate of reactions requiring protonation or acid catalysis in such environments.

In general, for both naturally occurring compounds and pollutants,

1. Hydrophobically bound adsorbates are most strongly bound;
2. Cationic adsorbates are next most strongly bound;
3. Anionic species are most weakly bound.

Uptake by clays of charged organic materials is termed **hydrophilic sorption**. As an example, an organic cation like the herbicide paraquat (**1**) is very readily

taken up by clays, despite its high solubility in water, because of these strong electrostatic interactions. There is also a possibility of weak adsorption of anions by "bridging cations." By this mechanism, anionic compounds like some proteins, carboxylic acids, and humic materials may be associated near the water-solid inter-

face. Generally, however, the direct uptake of cations by clays is much more important than the indirect (bridging) uptake of anions.

Mention should also be made of another weak mechanism of indirect uptake of strongly hydrogen-bonding materials. Water molecules are quite strongly oriented in the vicinity of certain clays because of attraction between the lone pairs on the oxygen atom of water and the positive charges on cations at the clay surface. This means that an excess of hydrogen atoms will be facing out into solution, and in the presence of molecules with lone pairs (hydroxyl groups, ether oxygen, carbonyl groups, etc.), hydrogen bonding will occur (Figure 1.2), and through these "water bridges," these molecules may, in favorable cases, build up to quite a high degree of adsorption.

Another general type of uptake of organic molecules by solid surfaces is called **hydrophobic sorption**. This interaction is quite general for natural sediments and soils, and leads to a high degree of concentration of hydrophobic material near the interface. Hydrophobic adsorption is strongly correlated with the organic carbon content of the sediment or soil. It has elements of partitioning; many investigators have, in fact, shown a very clear correlation between the extent of uptake of a chemical by a natural solid phase and the **partition coefficient**, K_p , of the chemical; that is, its ratio of concentration or activity between an organic solvent, often octanol, and water:

$$K_p = [\text{solvent}]/[\text{water}] \quad (1.6)$$

The partition coefficient is not the same as the ratio of the solubilities of a chemical in the two pure solvents, because at equilibrium the solvent phase contains some water and the water phase contains some solvent. Values of K_p sometimes vary with solute concentration, but are seldom much affected by temperature.

Many data are specifically available on the octanol/water partition coefficients (K_{ow}) of organic molecules (see, for example, Tewari et al., 1982; Miller et al., 1984, and Lyman, 1990a), and it has been repeatedly demonstrated that chemicals with high K_{ow} 's are very readily sorbed by natural sediments. For example, the extremely nonpolar compound DDT has a K_{ow} of about 10^6 (it is a million times more soluble in octanol than in water), and it is almost completely associated with the solid phase in a two-phase water-sediment system. For atrazine, a chemical of intermediate polarity, the K_{ow} is still high (3×10^3), but far less than that for DDT, so the extent of

Figure 1.2. A water bridge, showing how hydrogen bonding may assist in bringing certain organic molecules into the vicinity of clay surfaces.

association with sediments would be expected to be far less pronounced. For quite polar organic compounds, such as acetic acid, the octanol-water partition coefficient is far lower (0.5), and the distribution in the two-phase system would favor water. Because soil organic matter is so highly oxidized, current thinking is that it must have extensive nonpolar regions, perhaps alkyl chains, that are responsible for the partitioning (see Section 1.B.3c). (The quantity K_{ow} has also been shown to correlate well with other environmental parameters that depend on distribution between hydrophobic and aqueous phases, such as bioconcentration in aquatic organisms, uptake by mammalian skin, water solubility, and toxicity within a given series of compounds; Verschuieren, 1983).

For soils and sediments of differing organic matter content, the useful concept of K_{oc} has been introduced; this form of the partition coefficient makes the simplifying assumption that only the organic carbon is active in the sorption process, and the partition coefficient expression can be rewritten

$$K_{oc} = K_p / [\text{fraction organic carbon}] \quad (1.7)$$

Values of K_{oc} for selected chemicals have been tabulated (Lyman, 1990b). Data for many herbicides and polycyclic organic compounds (Walker and Crawford, 1968; Hassett et al., 1980) have confirmed the general applicability of this expression. However, at low organic carbon concentrations, such as are found in sandy soils and some clays, sorption still occurs for many chemicals, and the above equation does not fit the data particularly well.

Octanol-water partitioning and aqueous solubility are closely related, and one can be predicted fairly accurately from the other using a relationship devised by Mackay et al. (1980):

$$\ln K_{ow} = 7.494 - \ln C_w \quad (1.8)$$

where C_w is the water solubility in moles/L. Many other forms of this equation have been promulgated (cf. Lyman, 1990a) that appear to predict solubility more or less accurately for a given series of compounds.

At equilibrium, the uptake of a dissolved compound can often be expressed in the simple terms of the Freundlich isotherm equation,

$$[A]_s = K_p [A]_w^{1/n} \quad (1.9)$$

where $[A]_s$ and $[A]_w$ are, respectively, concentrations of the compound in the solid and water phase; K_p is an appropriate partition coefficient; and $1/n$ is an empirical exponential factor, often close to 1.0. Achievement of equilibrium, however, is often difficult to measure in studies with natural soils or sediments; kinetics of uptake may be complex, with a fraction of the solute rapidly taken up and a residual uptake period that may last for days or weeks. Pollutant uptake and release (desorption) kinetics are dependent on particle chemical characteristics, mass transfer properties for the solute in the sorbent phase, aggregation state of particles, and ability of the

solid state to swell or shrink after incorporation of organic matter (Karickhoff, 1984; Karickhoff and Morris, 1985).

3. Transformation of Organic Compounds

a. Reaction Mechanisms

The transformation of organic chemicals most often occurs in several molecular events referred to as *elementary reactions*. An elementary reaction is defined as a process in which reacting chemical species pass through a single transition state without the intervention of an intermediate. A sequence of individual elementary reaction steps constitutes a *reaction mechanism*. For example, the overall reaction for the hydrolysis of a Schiff base is written:

The reaction mechanism for this seemingly simple reaction is in fact quite complex, and is composed of four elementary reactions (Cordes and Jencks, 1963).

A reaction mechanism is actually a hypothesis or model that has been constructed from experimental evidence. As new experimental evidence is obtained, changes in the proposed reaction mechanism may be required. Chemical kinetics is probably the most powerful tool for the investigation and development of reaction mecha-

nisms. The consistency of a reaction mechanism can be verified in the laboratory by determining the dependence of reaction rates on concentration.

Once a reaction mechanism consisting of a sequence of individual elementary reactions has been proposed it is possible to develop rate equations, which predict the dependence of the observed reaction rate on concentration. The *principle of mass action*, which states the rate at which an elementary reaction takes place is proportional to the concentration of each chemical species participating in the molecular event, is used to write differential rate equations for each elementary reaction in the proposed reaction mechanism. The goal is then to obtain explicit functions of time, which are referred to as integrated rate laws, from these differential rate equations. For simple cases, analytical solutions are readily obtained. Complex sets of elementary reactions may require numerical solutions.

It is useful to classify elementary reactions according to their molecularity, which is defined as the sum of the exponents appearing in a rate equation for a single elementary reaction. The term *unimolecular reaction* is used to describe an elementary reaction involving one chemical species. A *bimolecular reaction* involves the interaction of two chemical species. The interaction of three chemical species, or a *termolecular reaction*, is quite rare and will not be considered for further discussion. Molecularity is often confused with the *order* of a reaction, which refers to the sum of the exponents appearing in an experimental rate equation.

b. Kinetics

Rate expressions. Initially, to determine how rate equations are developed from a proposed reaction mechanism, we will consider simple reaction mechanisms consisting of only one elementary reaction. For example, the differential rate equation for the hypothetical reaction in Equation 1.15

can be written as

$$-d[A]/dt = k_1[A] \quad (1.16)$$

For experimental determination of k , the integrated form of Equation 1.16 is conveniently written

$$[A] = [A]_0 e^{-kt} \quad (1.17)$$

or

$$\ln A = \ln A_0 - kt \quad (1.18)$$

Thus a plot of $\ln A$ versus t should be linear for a first order reaction with a slope of $-k$, which has units of time^{-1} , and a y-intercept of $[A]_0$. When experimental data

obtained in the laboratory are in close agreement with this theoretical expectation, we can say that the reaction obeys first-order kinetics. This allows us to speak of an experimental rate law as opposed to a theoretical rate law based on mechanistic considerations.

When comparing the reactivity of chemicals, it is convenient to speak in terms of the half-life ($t_{1/2}$) of a reaction or the time for 50% of the chemical to disappear. For first-order reactions, if we set $[A] = 1/2[A]_0$, and substitute into Equation 1.18, the expression for $t_{1/2}$ becomes:

$$t_{1/2} = 0.693/k \quad (1.19)$$

The half-life for a first-order reaction, therefore, is independent of the initial concentration of the chemical of interest.

For the more complex reaction containing two reacting chemical species, A and B (Equation 1.20)

the rate of disappearance of A is given by Equation 1.21.

$$d[A]/dt = k_2[A][B] \quad (1.21)$$

The integrated form of Equation 1.21 is:

$$\ln[(B_0 - A)/(A_0 - B)] = k_2 t(A_0 - B_0) \quad (1.22)$$

Thus for bimolecular reactions, plotting $\ln[B_0(A)/A_0(B)]$ versus t gives a line with slope $k_2(A_0 - B_0)$.

If one of the concentrations of a chemical species in a second-order reaction is present in excess, and as a result does not effectively change during the course of the reaction, the observed behavior of the system will be first order. Such a system is said to follow pseudo-first-order kinetics. If the concentration of the chemical species B in Equation 1.20 were in large excess of A, the disappearance of A could be written as:

$$d[A]/dt = k_{\text{obs}}[A] \quad (1.23)$$

where

$$k_{\text{obs}} = k_2[B] \quad (1.24)$$

Reaction mechanisms for the transformation of organic chemicals usually involve several elementary reactions. The kinetic expressions resulting from such mechanisms can become quite complex and difficult to handle. Often, simplifying assumptions can be used to analyze these systems. We shall examine one simplifying as-

sumption referred to as the *steady-state approximation*. It can be illustrated with the hypothetical reaction scheme:

If B is a reactive, unstable species its concentration will remain low. Applying the steady-state assumption, we assume that the rate of formation of the reactive species is equal to its rate of destruction:

$$k_1[A] = k_{-1}[B] + k_2[B] \quad (1.27)$$

Solving for the steady-state concentration of B, we find that:

$$[B] = k_1[A]/(k_{-1} + k_2) \quad (1.28)$$

If we assume that the conversion of B to C is *rate-limiting* or the *rate-determining step*, the overall rate of the reaction will be:

$$d[C]/dt = k_2[B] \quad (1.29)$$

Substituting the term for the steady-state concentration of B (Equation 1.28) into Equation 1.29 gives:

$$d[C]/dt = (k_2k_1[A])/(k_{-1} + k_2) \quad (1.30)$$

If the experimental rate law was determined to be $d[C]/dt = k_{\text{obs}}[A]$, then k_{obs} would be related to the elementary reaction rate constants by:

$$k_{\text{obs}} = k_2k_1/(k_{-1} + k_2) \quad (1.31)$$

Arrhenius equation. The measurement of rate constants in the laboratory for transformation processes that are exceedingly slow ($t_{1/2}$ on the order of months to years) can be quite difficult. To circumnavigate this problem, kinetic measurements are made at elevated temperatures to accelerate reaction kinetics. Of course, it is then necessary to extrapolate measured rate constants to environmentally significant temperatures. The temperature dependence of observed rate constants is given by the Arrhenius equation:

$$k_{\text{obs}} = A \exp(-E_a/RT) \quad (1.32)$$

where A is the *preexponential factor*, E_a is the activation energy, R is the gas constant, $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$, and T is the temperature in degrees Kelvin. From the logarithmic form of the Arrhenius equation it is apparent that the preexponential term A and the energy of activation E_a can be calculated from logarithms of the observed rate constants versus the reciprocal of the absolute temperatures. In the absence of experimental data to calculate E_a , a useful approximation for extrapolation is that rate constants will vary by a factor of 10 for each 20°C change in temperature. This corresponds to an activation energy of 20 kcal/mol .

c. Linear Free Energy Relationships

Correlation Analysis. Numerous empirical models have been developed in organic chemistry that describe relationships between structure and reactivity. The most successful and intensively investigated are the linear free energy relationships (LFER), which correlate reaction rate constants and equilibrium constants for related sets of reactions. As Hammett stated: "From its beginning the science of organic chemistry has depended on the empirical and qualitative rule that like substances react similarly and that similar changes in structure produces similar changes in reactivity" (Hammett, 1970). "Linear free energy relationships constitute the quantitative specialization of this fundamental principle" (Chapman and Shorter, 1970). The origin of the LFER can be better understood by considering the relationship between the changes in free energy involved in the kinetic and equilibrium processes. If two reactions exhibit a LFER, we can write:

$$\log k - \log k_o = m(\log K - K_o) \quad (1.33)$$

Substituting for k and K with the appropriate terms for free energy of activation (from transition-state theory) and free energy of reaction gives:

$$-\Delta G^\ddagger/2.3RT + \Delta G_o^\ddagger/2.3RT = m(-\Delta G/2.3RT + \Delta G_o/2.3RT) \quad (1.34)$$

$$-\Delta G^\ddagger + \Delta G_o^\ddagger = m(-\Delta G + \Delta G_o) \quad (1.35)$$

$$\Delta\Delta G^\ddagger = m\Delta\Delta G \quad (1.36)$$

From this analysis, it is apparent that a relationship between k and K (at constant temperature) is essentially a relationship between free energies. The LFER therefore indicates that the change in free energy of activation ($\Delta G^\ddagger$) exerted by a series of substituents is directly proportional to the change in free energy of reaction (ΔG).

The use of LFERs constitutes one of the most powerful means for the elucidation of reaction mechanisms. LFERs also provide us a means to predict reaction rates or bioactivity from more easily measured equilibrium constants such as octanol-water partition coefficients (K_{ow}), ionization constants (K_a), or acidity constants (K_{HB}). Brezonik (1990) has summarized the major classes of LFERs applicable to reactions in aquatic ecosystems (Table 1.2). These empirical correlations pertain to a variety

Table 1.2. Major Classes of LFERs Applicable to Reactions in Aquatic Systems

Relationship	Types of Reaction or Reactants	Basis of LFER
Brønsted	Acid- or base-catalyzed reactions: hydrolysis, dissociation, association	Rate related to K_a or K_b of product or catalyst
Hammett (sigma)	Reactions of para- or meta-substituted aromatic compounds: hydrolysis, hydration of alkenes, substitution, oxidation, enzyme-catalyzed oxidations; some photooxidations	Electron withdrawal and/or donation from/to reaction site by substituents on aromatic rings via resonance effects
Taft	Hydrolysis and many other reactions of aliphatic organic compounds	Steric and polar effects of substituents
Marcus	Outer-sphere electron exchange reactions of metal ions, chelated metals, and metal ion oxidation by organic oxidants such as pyridines and quinones	The three components of energy needed to produce transition state; for related redox reactions, $\ln k$ proportional to E°

of transformation processes, including hydrolysis, nucleophilic substitution, reduction, and oxidation.

Hammett equation. One of the first methods for relating structure and reactivity was developed by Hammett (1937). Hammett found that the reactivities of benzoic acid esters were directly related to the ionization constants, K_a , of the corresponding benzoic acids (Figure 1.3). Using substituted benzoic acids as his standard reference reaction, Hammett developed a LFER in the form:

$$\log(k_x/k_o) = \rho \log(K_x/K_o) \quad (1.37)$$

where O denotes unsubstituted benzoic acid and x denotes differently X-substituted benzoic acids in the m- and p-positions and ρ is the *reaction constant*. Hammett defined the log of the ratio of the ionization constants as a *substituent constant*, σ ,

$$\sigma_x = \log(K_x/K_o) \quad (1.38)$$

Substitution of Equation 1.38 into Equation 1.37 gives Equation 1.39:

$$\log(k_x/k_o) = \rho \sigma_x \quad (1.39)$$

Figure 1.3. Correlation of acid dissociation constants of benzoic acids with rates of alkaline hydrolysis of ethyl benzoates. Reprinted from Hammett (1937) by permission of the American Chemical Society.

Values for the substituent constant, σ , have been determined for a large number of substituent groups by measurement of the dissociation constant of the substituted benzoic acids. Select values of σ_m and σ_p for substituents in the meta- and para-positions, respectively, are summarized in Table 1.3. These substituent groups perturb the electron density at the reactive center through resonance, inductive, or field effects. In principle, σ values are independent of the nature of the reaction that is being investigated. The Hammett equation does not apply to ortho substituents because these groups may affect the reaction center through steric interactions. The sign of σ reflects the effect that a particular substituent has on developing charge at the reactive site. Electron-withdrawing substituents have positive values and electron-donating substituents have negative values.

The value of ρ for the ionization of benzoic acids, the standard reaction, is arbitrarily assigned a value of 1. The value of ρ for a given reaction is determined from the slope of the line of a plot of $\log(k_x/k_0)$ versus σ . A straight line indicates that the linear free energy of Equation 1.39 is valid. The magnitude of ρ reflects the susceptibility of a reaction to substituent effects. The sign of ρ is of diagnostic value because it indicates the type of charge development in the transition state for the rate limiting step. Reactions with negative ρ values (e.g., the hydrolysis of benzyl chlorides: Table 1.4) have positive charge development occurring in the transition state. Accordingly electron-donating substituents will stabilize the transition state, result-

Table 1.3. Substituent Constants^a

Substituent Group		σ_m	σ_p	σ^+	σ_t	F	R
Acetamido	AcNH	0.21	-0.01	-0.25		0.47	-0.27
Acetoxy	AcO	0.39	0.31	0.18		0.68	-0.07
Acetyl	Ac	0.38	0.50	0.57	0.28	0.53	0.20
Amino	NH ₂	-0.16	-0.66	-1.11	0.13	0.04	-0.68
Bromo	Br	0.39	0.23	0.02	0.45	0.72	-0.18
<i>t</i> -Butyl	(Me) ₃ C	-0.10	-0.20	-0.28		-0.10	-0.14
Chloro	Cl	0.37	0.23	0.04	0.47	0.69	-0.16
Cyano	CN	0.56	0.66	0.67	0.56	0.85	0.18
Ethoxy	EtO	0.10	-0.24	-0.58		0.36	-0.44
Ethyl	Et	-0.07	-0.15	-0.22		-0.07	-0.11
Fluoro	F	0.34	0.06	-0.25	0.52	0.71	-0.34
Hydrogen	H	0.00	0.00	0.00	0.00	0.00	0.00
Hydroxy	OH	0.12	-0.37	-0.85	0.30	0.49	-0.64
Methoxy	MeO	0.12	-0.27	-0.65	0.30	0.41	-0.50
Methyl	Me	-0.07	-0.17	-0.26	-0.05	-0.05	-0.14
Nitro	NO ₂	0.71	0.78	0.74	0.63	1.11	0.16
Phenyl	Ph	0.06	-0.01	-0.08		0.14	-0.09
Trifluoromethyl	CF ₃	0.43	0.54	0.58	0.42	0.63	0.19
Trimethylammonio	(Me) ₃ N ⁺	0.88	0.82	0.64	0.90	0.146	0.00

^aSources: C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.* 90, 4328 (1968), and P. R. Wells, *Linear Free Energy Relationships*, Academic Press, New York, 1968.

Table 1.4. Reaction Constants^a

Reaction	ρ
$\text{ArCO}_2\text{H} \rightleftharpoons \text{ArCO}_2^- + \text{H}^+$, water	1.00
$\text{ArCO}_2\text{H} \rightleftharpoons \text{ArCO}_2^- + \text{H}^+$, EtOH	1.57
$\text{ArCH}_2\text{CO}_2\text{H} \rightleftharpoons \text{ArCH}_2\text{CO}_2^- + \text{H}^+$, water	0.56
$\text{ArCH}_2\text{CH}_2\text{CO}_2\text{H} \rightleftharpoons \text{ArCH}_2\text{CH}_2\text{CO}_2^- + \text{H}^+$, water	0.24
$\text{ArOH} \rightleftharpoons \text{ArO}^- + \text{H}^+$, water	2.26
$\text{ArNH}_3^+ \rightleftharpoons \text{ArNH}_2 + \text{H}^+$, water	3.19
$\text{ArCH}_2\text{NH}_3^+ \rightleftharpoons \text{ArCH}_2\text{NH}_2 + \text{H}^+$, water	1.05
$\text{ArCO}_2\text{Et} + ^-\text{OH} \rightarrow \text{ArCO}_2^- + \text{EtOH}$	2.61
$\text{ArCH}_2\text{CO}_2\text{Et} + ^-\text{OH} \rightarrow \text{ArCH}_2\text{CO}_2^- + \text{EtOH}$	1.00
$\text{ArCH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{ArCH}_2\text{OH} + \text{HCl}$	-1.31
$\text{ArC}(\text{Me})_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{ArC}(\text{Me})_2\text{OH} + \text{HCl}$	-4.48
$\text{ArNH}_2 + \text{PhCOCl} \rightarrow \text{ArNHCOPh} + \text{HCl}$	-3.21

^aSource: P. R. Wells, *Linear Free Energy Relationships*, Academic Press, New York, 1968, pp. 12, 13.

ing in an acceleration of the reaction rate. On the other hand, electron-withdrawing groups will inhibit the rate of reaction by destabilizing the transition state.

Taft equation. Taft (1956) has extended the Hammett-type correlation to aliphatic systems. Because steric effects of substituents in aliphatic systems cannot be ignored as they were for *m*- and *p*-substituted benzene compounds, Taft recognized the need to develop separate terms for the polar and steric effects for substituent constants. Based on the observation that the acid-catalyzed hydrolysis of meta- and para-substituted benzoic acid esters are only slightly affected by the electronic nature of the substituent group (ρ values are near 0), Taft concluded that the acid-catalyzed hydrolysis of aliphatic esters would also be insensitive to polar effects of substituent groups. Any effect on rate due to substituent groups could therefore be attributed to steric effects. Taft defined a *steric substituent constant*, E_s , by:

$$E_s = \log(k_x/k_o)_A \quad (1.40)$$

where k_x and k_o are the hydrolysis rate constants for $XCOOR$ and CH_3COOR , respectively, and the subscript A denotes acid-catalyzed hydrolysis. The large ρ values measured for basic hydrolysis of benzoate esters demonstrates that the polar effects of substituents cannot be ignored. Assuming that the steric demands of the transition states for the acid- and base-catalyzed hydrolysis of esters are approximately equal, the polar parameter, σ^* , can be defined by:

$$\sigma^* = (\log(k_x/k_o)_B - \log(k_x/k_o)_A)/2.48 \quad (1.41)$$

where B denotes base-catalyzed hydrolysis and the factor 2.48 is used to normalize σ^* to Hammett's σ . The general Taft equation for LFERs in aliphatic systems (Pavelich and Taft, 1957) can then be written as:

$$\log(k_x/k_o) = \sigma^*\rho^* + \delta E_s \quad (1.42)$$

Several E_s and σ^* constants are listed in Table 1.5.

Not many environmentally oriented investigations have applied the Taft equation to the treatment of their results. One of the few such studies that have been reported is actually not on a purely aliphatic system. Based on the general Taft equation (1.42), Wolfe et al. (1980b) established a LFER for the alkaline hydrolysis of phthalate esters that is described by:

$$\log k_{OH} = 4.59\sigma^* + 1.52E_s - 1.02 \quad (1.43)$$

This LFER has been useful for the environmental assessment of phthalate esters for which hydrolysis rate constants have not been measured (Wolfe et al., 1980a).

Table 1.5. Steric and Polar Parameters for Aliphatic Systems^a

X	E_s	σ^*
H	+ 1.24	+ 0.49
CH ₃	0.00	0.00
CH ₃ CH ₂	- 0.07	- 0.10
<i>i</i> -C ₃ H ₇	- 0.47	- 0.19
<i>t</i> -C ₄ H ₉	- 1.54	- 0.30
<i>n</i> -C ₃ H ₇	- 0.36	- 0.115
<i>n</i> -C ₄ H ₉	- 0.39	- 0.13
<i>i</i> -C ₄ H ₉	- 0.93	- 0.125
<i>neo</i> -C ₅ H ₁₁	- 1.74	- 0.165
ClCH ₂	- 0.24	+ 1.05
ICH ₂	- 0.37	+ 0.85
Cl ₂ CH	- 1.54	+ 1.94
Cl ₃ C	- 2.06	+ 2.65
CH ₃ OCH ₂	- 0.19	+ 0.52
C ₆ H ₅ CH ₂	- 0.38	+ 0.215
C ₆ H ₅ CH ₂ CH ₂	- 0.38	+ 0.08
CH ₃ CH = CH	- 1.63	+ 0.36
C ₆ H ₅	- 2.55	+ 0.60

^aSource: J. Shorter, *Quarter. Rev.* (London), 24:423 (1970).

B. OVERVIEW OF THE ENVIRONMENT

In this section, we will attempt to provide background information that sets the stage for an analysis of the occurrence of environmental organic reactions. Environmental milieux are highly variable in their temperatures, pressures, oxygen content, etc., and reactions that are important in one medium such as the gas phase of the atmosphere may be negligible in another, such as bottom sediments. The section will begin with an overview of the atmosphere and its organic constituents, followed by brief surveys of the organic environments of surface and groundwaters, and of soils and sediments. Emphasis will be on the characteristics of the matrices and the organic materials associated with them; details on the reaction pathways, followed by some of the organic constituents, will be discussed in later chapters.

1. The Troposphere and the Stratosphere

Today's atmosphere is the product of thousands of millions of years of evolution; it has changed almost completely since the primeval atmosphere first formed. The evolution of the atmosphere is, of course, continuing. Although the rates of change

of major atmospheric constituents are very small, significant changes in some minor components are occurring now. For example, the activities of humans over the past century or so have caused a host of novel organic compounds to enter the atmosphere, and the combustion of huge quantities of fossil fuels has significantly increased its CO₂ content. Since the late 1960s, it has become clear that the entire troposphere is a transport system for trace organic compounds, as well as a gigantic reactor where chemical changes in those compounds are taking place under the influence of sunlight and in the presence of highly reactive intermediates.

a. The Thermal Structure of the Atmosphere

Virtually all (99.999%) of the mass of the earth's atmosphere lies within 80 km of its surface; 80% is within the lowest 12 km. The atmosphere is not a region of smoothly varying properties, but is distinctly stratified.

The traditional classification of atmospheric regions is based on temperature (Figure 1.4). Closest to the earth lies the **troposphere** (Greek *tropos*, change), a region of generally declining temperature in the upward direction. The cause of this thermal effect is the conversion of visible sunlight radiation at the earth's surface to heat (infrared) radiation. At about 10–12 km, a temperature minimum of approximately 210°K is reached; this is generally considered the top of the troposphere or **tropopause**. From 10 to about 50 km (the **stratosphere**) the temperature increases to about 270°K. Little organic chemistry occurs above 50 km. The region from 50 to 90 km (the **mesosphere**) is a region of generally declining temperatures, and finally, at still higher elevations (the **thermosphere**), the temperature increases sharply, to a maximum of about 2000°K at a few thousand kilometers.

The stratosphere is heated, principally, by a strongly exothermic, photochemically-driven reaction sequence;

The sequence is initiated by the homolysis of molecular oxygen. Light with wavelengths shorter than about 240 nm is virtually all absorbed by constituents of the upper regions of the atmosphere such as molecular N₂; however, at the top of the stratosphere the concentration of O₂ becomes sufficiently great for Reaction 1.44 to become important. The product of this reaction is two atoms of oxygen, which combine with molecular oxygen exothermically (in the presence of a third body, usually N₂), to produce ozone. (Ozone also reacts with oxygen atoms in a very exothermic reaction that returns two equivalents of O₂.) Molecular ozone, in turn, absorbs 240–290 nm actinic radiation to regenerate oxygen molecules and atoms.

Figure 1.4. Thermal and pressure profiles of the atmosphere with elevation above the earth's surface. From B. J. Finlayson-Pitts and J. N. Pitts, Jr., *Atmospheric Chemistry*, John Wiley & Sons 1986. Reprinted by permission.

The concentration of ozone is at a maximum at about 25 km, roughly in the middle of the stratosphere.

The stratosphere, unlike the troposphere, undergoes little vertical mixing and few clouds are present; therefore, molecules that reach the stratosphere (SO_2 from volcanic eruptions, chlorofluorocarbons, etc.) tend to remain there for some time and are not "rained out" (deposited back to the earth's surface) as compounds in the troposphere can be.

b. Solar Energy Distribution

The sun emits radiation whose frequency distribution is closely similar to that predicted for a blackbody radiator at 5900°K (Figure 1.5). It essentially begins in the vacuum UV at about 120 nm, rises to a maximum at 400 nm at the beginning of the visible spectrum, and falls gradually through the visible and infrared regions. The total amount of solar energy received at the earth's surface is about 1370 J/m²/sec, and a quantity approximately equal to this is either reflected back into space or absorbed by the atmosphere.

Diurnal and seasonal variations in solar intensity are, of course, of utmost importance to ecosystems. In the extreme polar regions there is no direct solar radiation at all for more than four months of the year, whereas near the equator the overall intensity of sunlight fluctuates less than 10% annually. The spectral energy distribution also varies with the season. For example, in July in the middle latitudes (ca. 40°), the fraction of shorter-wave UV (290–315 nm) in the total solar radiation is more than three times higher than it is in December, due to the shorter path these easily scattered wavelengths have to traverse through the atmosphere. For similar reasons, shortwave UV is more intense at high elevations, particularly in the tropics where stratospheric ozone is less concentrated (Caldwell et al., 1980).

Because several constituents of the atmosphere (O₃, O₂, CO₂, and water) have

Figure 1.5. Energy flux (in watts per square meter) plotted against wavelength, calculated for a 6000°K blackbody radiator, and compared to the observed solar flux at sea level and outside the earth's atmosphere. Reprinted from Chapter 16, "Thermal Radiation," in *Handbook of Geophysics*, U.S. Air Force Cambridge Research Center, 1960.

important absorption maxima in various regions of the solar spectrum, the frequency distribution of radiation at the earth's surface differs significantly from that emitted by the sun. Water, in the form of cloud droplets, for example, absorbs energy in the IR region and also reflects and scatters other sunlight wavelengths, so that the earth's surface is cooled when it is present in high concentrations. Other particles in the atmosphere also absorb and scatter incoming light in a complex manner that depends on their size, shape, and composition.

Because tropospheric CO₂ levels have been increasing due to fossil fuel combustion over the past 100 or so years, it has been theorized that more and more infrared radiation is being absorbed, warming the troposphere (the so-called greenhouse effect). Other IR-absorbing atmospheric gases such as CH₄, nitrous oxide, and chlorofluorocarbons also appear to be important contributors to the hypothesized global warming (Ramanathan et al., 1985; Rowland, 1989; Lashof and Ahuja, 1990). Tropical deforestation also has been implicated in global CO₂ increases, since when trees are cut down, the succeeding grassy or weedy plant community can remove only a small fraction of atmospheric CO₂, compared to the forest. Furthermore, much of the wood obtained is burned, adding to the CO₂ burden directly.

In addition, stratospheric ozone concentrations appear to be declining, due to photolysis by shortwave UV of volatile chlorine-containing compounds such as CFCl₃ and its relatives (Reaction 1.48); the Cl atoms produced in this reaction scavenge O atoms (Reaction 1.49) and

catalyze an efficient chain process (Reaction 1.6) that removes ozone molecules and converts them to oxygen molecules (Molina and Rowland, 1974; Rowland, 1989; Rowland, 1991):

These compounds reach the stratosphere because they are so unreactive in all tropospheric processes, including reactions with HO· to which they are virtually inert. Measurements of atmospheric ozone in Antarctica (Stolarski et al., 1986), in the Arctic (Zurer, 1990), and even in the temperate latitudes (Watson et al., 1988) all point to a decrease in stratospheric ozone concentrations. Recent attempts to diminish the use of ozone-depleting compounds on a global basis appear to have been successful; however, only minor effects on the rate of ozone destruction are likely to be observed for many years to come.

c. Chemical Constituents and Their Reactions

The reactions leading to the transformation of organic compounds in the atmosphere are primarily oxidations; their rates are governed by the reactivities of the various classes of organic substances toward the oxidants (typically reactive oxygen-containing species) present. The majority of these oxygenated forms and the mechanisms of their reactions are discussed in detail in Chapter 4. Only an overview will be presented in this section.

Although a great assortment of organic molecules is present in the troposphere at all times, most occur only in trace concentrations. Because of the enormous extent of the atmosphere, however, it can be a sink for huge quantities of a given compound. One part in 10^9 , over the whole of the atmosphere, would correspond to three million tons of a uniformly distributed substance.

A comprehensive list of organic compounds detected in both natural and polluted atmospheres has been compiled by Graedel (1978). The book consists principally of tables, listing more than 1,600 identified compounds by structural class, concentration, and atmospheric lifetime, if known. The tables include substances found in tobacco smoke, forest fires, volcanic eruptions, and industrial emissions.

Hydrocarbons. The simplest hydrocarbon, methane (CH_4), is also by far the most abundant organic species in the atmosphere. It is largely produced at or slightly below the earth's surface by biotic mechanisms such as the anaerobic microbial decomposition of organic matter in such places as marshes, lake bottoms, landfills, and the stomachs of ruminant animals. Other sources of CH_4 of probable lesser importance include natural gas seepages and incomplete combustion. Recent measurements of atmospheric methane concentration show that it has been increasing at about 1% per year, from typical levels of about 1.5 ppm measured 15 or so years ago, to about 1.75 ppm at present (Rasmussen and Khalil, 1983; Khalil and Rasmussen, 1990). The lifetime of methane in the atmosphere is almost completely determined by its reaction with hydroxyl radical; for details see Chapter 4.B.2. A possible decline in the global levels of atmospheric hydroxyl radicals has been postulated as a contributing reason for the increasing methane concentration (Khalil and Rasmussen, 1985), although these workers believe that increased emission from agricultural and industrial activities contribute the majority of the increased concentration observed.

Higher alkanes found in the atmosphere, sometimes included in a category called **nonmethane hydrocarbons** or NMHC, principally come from natural gas seepages, transportation, and industrial activities. Normally, either ethane or butane is the second most abundant aliphatic hydrocarbon in atmospheric samples [usually in the 50–100 ppb range, more than an order of magnitude lower in concentration than methane (Cavanagh et al., 1969; Altshuller, 1983)]. Higher alkanes (up to C_{40}) have been detected in aerosols and other atmospheric samples (Appel, 1981; Hutte et al., 1984; Sexton and Westberg, 1984; Harkov, 1986; Levsen et al., 1991). In clean environments, *n*-alkanes of odd carbon number from C_{23} to C_{33} predominate. The principal source of these compounds is the epicuticular wax layer of plants.

Branched-chain alkanes in the C_{24} – C_{30} range appear to be largely products of vehicular exhaust, and are apparently synthesized during fuel combustion (Boone and Macias, 1987).

Unsaturated aliphatic and cyclic hydrocarbons have numerous biological sources. Ethylene, $H_2C=CH_2$, the simplest of the series, is emitted by green plants in substantial quantities. It has hormonal activity and has been implicated in the control of many physiological processes in plants. The natural tropospheric concentration of ethylene is very low due to its high reactivity with ozone, $\cdot OH$, and other atmospheric oxidants (Robinson and Robbins, 1968), but in polluted atmospheres its concentrations can be much higher. It is a product of combustion of wood, coal, oil, natural gas, and petroleum. Elevated levels of ethylene, such as may occur in homes where coal gas is used for cooking, can be very deleterious to plants.

Green plants also release substantial quantities of isoprene (2) as well as monoterpenoid hydrocarbons such as α -pinene (3), myrcene (4), and limonene (5). These compounds contribute significantly to atmospheric organic concentrations in remote or forested areas (Altshuller, 1983; Hutte et al., 1984). It has been estimated that the global output of these substances may equal about 28% of the annual output of methane (Rasmussen and Went, 1965).

Aromatic hydrocarbons are produced anthropogenically and have been identified in urban air. Generally, toluene is the most abundant aromatic hydrocarbon; benzene concentrations range from $1/2$ to $2/3$ of that of toluene. Simple aromatic compounds such as xylenes and other alkylated benzenes have also been detected at much lower (0.001 to 0.010 ppm) concentrations (Wathne, 1983). The principal source of these compounds is probably gasoline fuel evaporation, but it has been shown that simple aromatic hydrocarbons can be produced by cracking higher condensed molecules. Diesel exhaust contains a high proportion of two-ring hydrocarbons such as naphthalenes, indans, and tetrahydronaphthalenes (Levins, 1972).

Polycyclic aromatic hydrocarbons (PAHs), defined as aromatic hydrocarbons with three or more rings, are also found in the atmosphere; they (especially the higher PAHs) are largely associated with particles. The mechanisms of formation of PAHs are discussed in Chapter 4. PAHs having fused ring numbers from two (naphthalene) to seven (coronene) have been observed (Lee et al., 1981; Hoff and Chan, 1987; Levsen et al., 1991). Concentration ranges reported are from less than 1 ng/m³ to hundreds of ng/m³. The combustion of almost any organic material produces PAHs (Table 1.6.) Benzo[a]pyrene (**6**), a particularly active carcinogenic PAH, has been identified repeatedly in urban air studies. Usually, PAH concen-

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trations are highest in winter months, showing that heating systems are the most important contributors of atmospheric PAH; but relatively large quantities are also produced by automobiles, electricity-generating stations, and refuse burning. Tobacco smoke and "tar" have especially high PAH concentrations; a heavy smoker probably inhales up to 1 µg of benzo[a]pyrene daily (Wynder and Hoffmann, 1968). The atmospheric reactions of PAH include oxidations, usually by hydroxyl radical, to give rise to phenols and quinones (König et al., 1983) and also reactions with nitrogen oxides (usually surface-catalyzed) to produce nitro-PAH derivatives (Pitts et al., 1978; Arey et al., 1986; Pitts, 1987).

Fuel-rich conditions and relatively low temperatures permit the processes of PAH formation to continue for a long enough period so that roughly spherical aggregates of organic particles of colloidal dimensions (soot) are produced. In practical terms, a PAH with a molecular weight of about 2,000 can be considered to be a soot particle (Miller and Fisk, 1987). These high-carbon particles are long-lived and appear to be transported over very considerable distances.

Table 1.6. Formation of PAH During Pyrolysis of Various Organic Compounds

Material Pyrolyzed	Benzo[a]pyrene Produced (µg/g)
Glucose	48
Fructose	98
Cellulose	289
Stearic acid	1200
Dotriacontane	3130
β-Sitosterol	3750

Source: Schmeltz and Hoffmann (1976).

Hazes in the Arctic have been systematically observed since the late 1970s. Known to contain high concentrations of sulfur oxides as well as carbon, they form in the late autumn when weather and temperature patterns are favorable for transport of sooty particles from the industrial regions of North America and Europe (particularly the former Soviet Union). During the winter, such hazes may cover a region approximating the size of North America and extending vertically to at least 9,000 m. In the spring, increasing atmospheric moisture and rain combine to scavenge and "rain out" the aerosols. It is probable that their carbon constituents may absorb 10% or more of the incident solar energy over the Arctic ice cap in the late winter months when their extent is greatest. The effects of these hazes on climate or on the Arctic ecosystem are almost entirely unknown (Hileman, 1983; Novakov, 1984).

Atmospheric particles are produced in virtually all combustion processes and are also formed when volatile products of plant origin are irradiated in the presence of a light-absorbing species such as NO_2 . The bluish atmospheric hazes common in forested mountainous areas have been attributed to the latter process. Traces of SO_2 also promote the formation of organic particulate material. These particles, entering the atmosphere, are the principal locus for PAHs.

Oxygen-containing organic compounds. Data on oxygenated species in the atmosphere are relatively scarce, principally due to the lack of suitable analytical procedures for the determination of polar constituents in the presence of a large excess of hydrocarbons. Interest in the area is increasing, however, because of evidence that many reactive oxygen-containing species (epoxides, lactones, and hydroperoxides, for example) may be important in the epidemiology of respiratory disorders and cancer.

Methanol and ethanol occur in crankcase emissions and have been detected in urban air, methanol at levels up to 0.1 ppm (Bellar and Sigsby, 1970). In addition, rather high concentrations of *n*-butanol (0.019 ppm) occurred in the air at Point Barrow, Alaska (Cavanagh et al., 1969); it is likely that biological activity was responsible. Phenol is present at a few thousandths of a ppm; nitrophenols have been detected in rain water (Nojima et al., 1976; Levsen et al., 1991). Alkylphenols and alkyl-substituted nitrophenols have been identified in urban aerosols and in the exhaust from internal combustion engines (Schuetzle et al., 1975; Kuwata et al., 1980).

Carbonyl compounds are probably present at low levels in all air samples (Fung and Grosjean, 1981). A great variety of combustion processes produce aldehydes; they are particularly abundant in wood smoke, and have also been identified in the products of combustion of natural gas and fuel oil, and in engine exhaust samples. It is likely that they are relatively long-lived intermediates in atmospheric photooxidation reactions. Formaldehyde (CH_2O), for example, is always an obligatory intermediate in the conversion of methane to CO_2 . In nearly all air samples so far examined, formaldehyde has been the most abundant aldehyde, with acetaldehyde, propionaldehyde, acrolein, benzaldehyde, crotonaldehyde, and furfural sometimes present at much lower concentrations (Kuwata et al., 1979; Penkett, 1982; Zhou and

Mopper, 1990; Levsen et al., 1991). In Los Angeles air, higher aldehydes have been reported to be present at concentrations comparable to those of formaldehyde. In rain, fog, and mist samples taken in California, formaldehyde and acetaldehyde were always present, but surprisingly high concentrations of glyoxal and pyruvaldehyde were also detected. One fog sample contained 276 μM (16 mg/L) of glyoxal. It was suggested that the α -dicarbonyl compounds were present at such high concentrations in the water because they were either more water-soluble or reacted more slowly with water or sulfur oxides than the monoaldehydes (Steinberg and Kaplan, 1984; Igawa et al., 1989). In Caribbean air samples, a series of aliphatic aldehydes ranging in chain length from C_1 to C_{18} was identified (Zhou and Mopper, 1990). A forested atmosphere in Colorado was shown to contain (in addition to formaldehyde and acetaldehyde) several higher aldehydes typical of higher plants, including 2-hexenal (**7**) and *p*-hydroxybenzaldehyde (**8**; Nondek et al., 1992). Naphthalene- and alkynaphthaldehydes, anthracene-9-carboxaldehyde (**9**) and phenanthrene-9-carboxaldehyde (**10**) were identified in diesel exhaust particle extracts, together with some of their alkylated homologs (Choudhury, 1982; Newton et al., 1982).

Not as much work has been reported on atmospheric ketone concentrations. Acetone was present at 0.001 ppm in the air at Point Barrow, Alaska (Cavanagh et al., 1969) and also, at half that concentration or less, in air over the Atlantic (Penkett, 1982; Zhou and Mopper, 1990); it is also present at higher elevations (Arnold et al., 1986). Phenyl and higher cyclic ketones, a few C_6 – C_{18} aliphatic ketones, butanone, biacetyl and 4-methyl-2-pentanone have also been identified in ambient air (Kawamura and Kaplan, 1983; Ramdahl, 1983; Zhou and Mopper, 1990). Several quinones have been identified by Soxhlet extraction of atmospheric particulate material, including anthraquinone and more complex multi-ring compounds (Choudhury, 1982; Ramdahl et al., 1982). In addition, more than 40 other oxygenated PAHs including aldehydes, ketones, lactones, and anhydrides have also been characterized from airborne particle extracts (Choudhury, 1982; Newton et al.,

1982; Ramdahl et al., 1982; König et al., 1983; Helmig et al., 1992). Fluorenone (11) and its alkyl homologs were particularly abundant in diesel emission particulate material.

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Carboxylic acids are produced in major quantities by the combustion of coal and wood. In fact, some time ago it was reported that far higher concentrations of organic acids than hydrocarbons were present in the volatile constituents from a large coal-fired power plant (Cuffe et al., 1964). However, the atmospheric fates of the acids are not completely understood. They do not appear to undergo important chemical reactions, except for keto acids, which photodegrade in a few hours (Grosjean, 1983; Berges and Warneck, 1992). Mostly, they are transferred back to the surface of the earth largely by dry deposition (if in the gas phase) and rainout (if in the particulate phase (Grosjean, 1989).

Formic acid is typically found at concentrations similar to those of the other one-carbon oxygenated compounds, methanol and formaldehyde. Other mono- and dicarboxylic acids are frequently identified in aerosols and other particles such as rain, fog, and mist; acetic acid is usually approximately as abundant as formic acid (Berkenbus, 1983; Kawamura and Kaplan, 1984; Kawamura et al., 1985; Steinberg et al., 1985; Harkov, 1986; Yokouchi and Ambe, 1986; Grosjean, 1989). Pyruvic acid, $\text{CH}_3\text{C}=\text{O}-\text{COOH}$, is produced during atmospheric oxidation of aromatic compounds such as *o*-cresol (Grosjean, 1984). It, like other keto acids, photodegrades further in sunlight to a mixture of products including formaldehyde, acetaldehyde, and PAN (Grosjean, 1983; Berges and Warneck, 1992).

Extracts of rain and snow from a southern Indiana location contained a long series of fatty acids, ranging in size from C_{12} to C_{28} . Concentrations of total acids ranged from 4 to 45 $\mu\text{g/L}$; palmitic and stearic acids (*n*- C_{16} and C_{18} , respectively) predominated. It was noted that concentrations of fatty acids were highest in the spring, when plant growth and pollen release were contributing organic matter to the atmosphere, and declined in the late autumn when deciduous plants died (Meyers and Hites, 1982). Analyses of atmospheric fallout samples in other areas have also revealed several long-chain fatty acids in the C_8 - C_{34} range, including unsaturated and branched-chain acids. Phenolic acids were also identified from a Japanese sample, including *o*-, *m*-, and *p*-hydroxybenzoic acids and several hydroxycinnamic acids. It was concluded that volatilization from pollens and other plant parts probably contributed to the occurrence of these compounds in the atmosphere (Matsumoto and Hanya, 1980; Levsen et al., 1991).

Carboxylic esters are very rarely found in atmospheric samples, with the exception of phthalate esters (12). These materials are practically ubiquitous in air and water

samples (Appel, 1981; Hoff and Chan, 1987). Dibutyl, dioctyl, and di(2-ethylhexyl) phthalates are produced in very large quantities for use as plasticizers, lubricants, and ingredients of inks, cosmetics, adhesives, and coatings. The compounds combine great oxidative and hydrolytic stability with low water solubility and relatively high vapor pressure, and thus enter and persist in the atmosphere.

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Novakov has suggested that "primary oxidants," hydrogen peroxide and organic hydroperoxides (as opposed to the "secondary oxidants" formed in photochemical smog episodes), may play important roles in atmospheric chemistry and may have significant biological effects. The intermediacy of peroxy radicals, of course, is well established (see Section 4.A.1) in atmospheric photooxidation reactions, but the role of relatively long-lived nonradical forms has not been fully explored. Both of these types of oxidants are formed when pure or mixed hydrocarbons are burned in internal combustion engines (Novakov, 1984). Hydroperoxides and peroxy acids such as peracetic acid, $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and hydroxymethyl hydroperoxide, HOCH_2OOH , have also been shown to be formed in laboratory studies from a variety of hydrocarbon and carbonyl compound precursors (Hanst and Gay, 1983; Hewitt and Kok, 1991). Methyl, hydroxymethyl, and hydroxyethyl ($\text{HOCH}_2\text{CH}_2\text{OOH}$) hydroperoxides have been detected in air (Heikes et al., 1987; Hellpointner and Gäb, 1989). The sum of the concentrations of methyl hydroperoxide, hydroxymethyl hydroperoxide, and three other organic peroxides, measured in ambient air sampling studies in Colorado, was found to approximate or slightly exceed that for hydrogen peroxide (Hewitt and Kok, 1991).

Other organic compounds. Volatile organic nitrogen compounds of natural origin include aliphatic amines such as methyl, dimethyl, ethyl, diethyl, *n*-propyl, isopropyl, *n*-butyl, and *sec*-butyl, which have been identified in cattle feedlot air (Mosier et al., 1973). Dimethylnitrosamine, which could be formed by reactions of secondary amines with nitrogen oxides in the air or have a terrestrial origin, has been detected in ambient air samples in urban areas (Epstein et al., 1976; Fine et al., 1976). A number of heterocyclic nitrogen compounds have been detected in the nanograms/ m^3 (parts per trillion) range, including caffeine, isoquinoline, and carbazole (Lee et al., 1981; Kawamura and Kaplan, 1983). Three nitriles (cyano compounds) derived from PAHs have been reported from urban air particles; unidentified isomers of acenaphthene-, anthracene-, and pyrenecarbonitriles (Ramdahl et al., 1982).

Sulfur compounds include alkylthiols (products of anaerobic microbial activity)

and dimethyl sulfide (Lovelock et al., 1972; Adams et al., 1981; Andrae and Raemdonck, 1983). Thiols are also by-products of pulp and paper bleaching operations. In polycyclic fractions, dibenzothiophene and a few related compounds have been identified (Lee et al., 1981). Several compounds containing both sulfur and oxygen have been reported, including monomethyl and dimethyl sulfate, methane-sulfonic acid (Panter and Penzhorn, 1980) and *bis*-hydroxymethyl sulfone, $\text{HOCH}_2\text{SO}_2\text{CH}_2\text{OH}$ (Eatough and Hansen, 1984; Eatough et al., 1986). The latter compound was proposed to be formed by a series of reactions involving ozone, ethylene, and SO_2 .

Atmospheric halogen compounds (Penkett, 1982) are of both natural and industrial origin. Probably the most abundant halocarbon in the troposphere is methyl chloride, CH_3Cl , which is present at a level of 0.6–2 parts in 10^9 . It appears to be present in volcanic emissions, formed by microbial fermentation, by the combustion of vegetation (Lovelock, 1975), and by the $\text{S}_\text{N}2$ reaction of methyl iodide (a constituent of marine algae) with the large excess of chloride ion in seawater (Zafiriu, 1975). Methyl iodide is also present in the atmosphere in highly variable amounts, averaging about one part in 10^{12} ; much higher concentrations are present in seawater (Lovelock et al., 1973). It is likely that other halogenated organic compounds of natural origin are also present in the atmosphere; for example, a host of Cl-, Br- and I-containing haloforms and a variety of other halogen compounds have been identified as algal metabolites (Burreson et al., 1975; Gschwend et al., 1985). Organohalogen compounds appear to be much more common in nature than was previously thought; Swedish workers have shown that the concentrations of halogen-containing organic compounds in 135 lakes in southern Sweden were comparable to those of polluted rivers such as the Rhine (Asplund and Grimvall, 1991). These authors rejected the hypothesis of long-range atmospheric transport and concluded that enzymatic halogenation reactions were the source of the bulk of the observed haloorganic compounds.

Other halogenated compounds detected in low concentrations (usually less than 0.03 part in 10^9) include chloroform (CHCl_3), dichloromethane (CH_2Cl_2), 1,1-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$), 1,1-dibromoethane or EDB ($\text{BrCH}_2\text{CH}_2\text{Br}$), 1,1,1-trichloroethane (CH_3CCl_3), trichloroethylene ($\text{ClCH}=\text{CHCl}_2$) and tetrachloroethylene ($\text{Cl}_2\text{C}=\text{CCl}_2$). Virtually all of these compounds have an anthropogenic origin and, in many cases, their tropospheric concentrations have been increasing (Tsani-Bazaca et al., 1982; von Dörseln and Thiemann, 1985; Prinn et al., 1987). EDB and 1,1-dichloroethane are added to motor fuels because of their antiknock properties; trichloroethylene, trichloroethane, and tetrachloroethylene are used as solvents or in dry cleaning operations. It is likely that a significant fraction of the atmospheric chloroform is volatilized from drinking water, cooling waters, and wastewaters which have been treated with aqueous chlorine (see Section 5.A.3; Barcelona, 1979). Chloroform and 1,2-dichloroethane are also produced in automobile exhaust (Harsch et al., 1977; Clark et al., 1982).

Polychlorinated biphenyls (PCBs: **13**) as well as DDT (**14**) and related compounds have been detected in air and atmospheric particle samples (Harvey and Steinhauer, 1974; Bidleman and Olney, 1974). Indoor air may contain rather high levels of

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PCBs. Many products once contained PCBs and were used primarily inside buildings, such as printing ink, carbonless carbon paper, small electrical capacitors, and fluorescent light ballasts. MacLeod (1981) showed that indoor PCB concentrations in offices, private homes, and laboratories were (in the early 1980s) at least 10x and often 100x higher than outdoor levels. She also sampled an office in which a fluorescent light ballast had burned out and noted that immediately after the burnout, concentrations rose to more than $10 \mu\text{g}/\text{m}^3$ and then fell gradually over a period of at least three months to more typical values of $200 \text{ ng}/\text{m}^3$.

Among the chlorinated heterocyclic compounds, chlorinated dibenzodioxins (**15**) and chlorinated dibenzofurans (**16**) have received much attention recently because of their high acute toxicity in some systems and their occurrence in the herbicide Agent Orange, in waste oils, and in bleached paper products. The compounds have been observed to be formed in low yields in many combustion-related processes such as municipal waste incineration (Rappe, 1984), and have been measured in ambient air samples by numerous investigators (see, e. g., Czuczwa and Hites, 1986; Marklund et al., 1986). Halogenated PAHs have been identified in flue gas effluents (Eklund and Stromberg, 1983).

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2. Natural Waters

The earth is unique in having a significant (ca. 70%) surface covering of liquid water. Table 1.7 summarizes the global distribution of surface and near-surface water. The oceans contain a very large majority of the terrestrial water; most of the remainder is glacial ice.

Almost all of the fresh liquid water is groundwater, with at least half of the total present at depths of greater than 1000 m. (Much less than 1% of the total is in the root zone of the soil.) Lakes and rivers, despite their extreme importance for humans, are a quantitatively insignificant component of the world's water supply. There is about as much water in the atmosphere as there is in all the world's rivers.

Evaporation and precipitation are in almost exact balance on a global basis. Of the rain and snow falling on land, about a third runs off and enters the ocean via river and lake drainage systems. The other two-thirds is retained temporarily by the

Table 1.7. Global Distribution of Water

	Volume (km ³)	%
Oceans	1.37×10^9	97.3
Ice caps, glaciers	3.0×10^7	2.1
Lakes	1.2×10^5	8×10^{-3}
Rivers	1.2×10^4	8×10^{-4}
Ground water	8.3×10^6	0.6
Soil moisture	2.5×10^4	1.8×10^{-3}
Atmosphere	1.3×10^4	9×10^{-4}
	1.41×10^9	100.0

soil and returned to the atmosphere directly (by evaporation) or indirectly (by transpiration from plants).

a. Water as Solvent and Reactant

Water is an angular molecule with an H-O-H bond angle of 104.5° and an O-H bond length of 0.96 Å. The energy of dissociation of the O-H bond is about 450 kJ/mol, much higher than that for typical C-C bonds which average around 350 kJ/mol.

Water has a very high latent heat of vaporization (2300 J/g, by far the highest of all common liquids), and accordingly, considerable energy must be supplied to the liquid to convert it to the vapor. Nevertheless, the atmosphere always contains water both in the vapor state and in the form of small aerosol droplets. At 20°C, up to 17 g water vapor/m³ can be held in the air.

Liquid water. The structure of liquid water is still controversial. Some models suggest that it can be represented as a slightly disordered ice, although these representations do not account very well for the remarkable degree of supercooling (up to 40°C) that the liquid can exhibit. It would be expected that ice-like assemblages would be efficient nuclei for crystallization.

An early proposal by Pauling (1960) was that liquid water could be considered a self-clathrate (Figure 1.6), with a central, nonhydrogen-bonded "guest" molecule surrounded by a hydrogen-bonded framework of pentagonally and hexagonally-faced polyhedra. This model appears to be somewhat too "ordered" to account for many of the properties of water (Frank and Quist, 1961), but its central idea of a structure incorporating both "framework" (hydrogen-bonded) and "interstitial" (nonhydrogen-bonded) water molecules has been included in many of the more recent attempts to describe liquid water. The "flickering cluster" model (Nemethy and Scheraga, 1964) has many adherents; it posits the existence of compact, short-lived assemblages of hydrogen-bonded molecules in equilibrium with unassociated, "vapor-like" water. Cluster models can be expressed as an equilibrium between two

Figure 1.6. Pauling's host-guest model for liquid water structure. The central water molecule is envisioned as not taking part in hydrogen bonding with the surrounding icosahedral assemblage of 20 fully hydrogen-bonded molecules. From J. L. Kavanau (1964), *Water and Solute-Water Interactions*. Reprinted by permission of Holden-Day, Inc.

forms of water; "bulky" water $(\text{H}_2\text{O})_b$ which is ice-like; that is, consisting of associated, open structures with considerable void space, and "dense" water $(\text{H}_2\text{O})_d$ which is more closely packed and less hydrogen-bonded. Cooling such an assemblage would cause a shift in the equilibrium toward the bulky form, which would eventually crystallize, whereas heating it would increase the proportion of dense water which would escape as vapor.

Water as a solvent. Aqueous solutions can be thought of as rearrangements of the structure of liquid water in order to accommodate foreign molecules, which can interact with the solvent in more or less consequential ways. Two extremes can be imagined; a virtual noninteraction in which the water molecules merely circumvent the solute, arranging themselves around it; and an almost complete incorporation, in which the functional groups of the solute molecule placidly combine in the hydrogen-bonded lattice of the solvent. The former extreme is approximated in solutions of aliphatic hydrocarbons; the second, in solutions of sugars and sugar alcohols.

The molar solubility of aliphatic hydrocarbon gases in water shows a maximum at $\text{C}_3\text{--C}_4$. This appears to represent the optimum size for a clathrate-like structure in which the host water molecules arrange themselves around the guest hydrocarbon. This is a good example of the so-called "hydrophobic interaction" or "like-dissolves-like" phenomenon. Presumably, larger cages, such as would be required to surround a larger molecule, are less stable. The negative entropy change that occurs when a

nonpolar gas is dissolved in water is quite considerable, suggesting that a more ordered, "ice-like" state results as the solute exerts a tendency for the water molecules in its vicinity to become more "bulky."

The properties of water in the presence of nonpolar solutes (those not having functional groups that can significantly interact with the water lattice) are to some degree similar to those of water containing nonpolar gases. Thus, for example, there is a roughly inverse linear relationship between the molar volume of a saturated hydrocarbon and its solubility. The aqueous solubilities of aliphatic hydrocarbons decrease sharply with increasing chain length, from about 5×10^{-4} M for *n*-pentane to 2.5×10^{-5} M for *n*-heptane and 1×10^{-7} M for *n*-dodecane (McAuliffe, 1966). It appears as if the formation of structured cavities having water molecules of sufficient size to accommodate hydrocarbons having more than a very few carbon atoms is energetically quite unfavorable.

Aromatic hydrocarbons also decrease in solubility with size, although they are far more soluble (approximately two orders of magnitude on a molar basis) than aliphatic hydrocarbons having the same number of carbon atoms (Mackay and Shiu, 1977; Pearlman et al., 1984). The solubilities of benzene, toluene, and naphthalene are, respectively, 1750 mg/L (0.022 M), 550 mg/L (6×10^{-3} M), and 32 mg/L (2.5×10^{-5} M). Even a rather large aromatic compound such as phenanthrene ($C_{14}H_{10}$) has a solubility of nearly $1 \mu\text{M}$. It is probable that there are significant charge-transfer interactions between water molecules and the pi electron clouds of aromatic species.

Striking increases in water solubility result when heteroatoms are introduced into hydrocarbon chains, due to the ability of the substituent to take part in hydrogen bonding and assume a position in the structural framework of the liquid. The solubility of *n*-hexane is only about 1×10^{-4} M, but that of di-*n*-propyl ether is about 2.5×10^{-2} M, and triethylamine is miscible with water. Introduction of polar or charged functional groups with exchangeable or ionizable hydrogens, such as -OH, -NH-, -SO₃⁻, or -COO⁻/-COOH, causes dramatic changes in solubility behavior; hydrophobic interactions become less important than the short-range, stronger interactions between the polar groups and water molecules, unless the polar group is contained in a molecule having extensive nonpolar regions (such as a long-chain alcohol). As an example, a short-chain alcohol such as *n*-butanol may participate in water clusters by forming up to three hydrogen bonds, using the hydrogen atom and two electron pairs on oxygen. The nonpolar end of the molecule is probably surrounded by a clathrate-like region similar to the solvation cages of *n*-alkanes. By analogy to hydrocarbons, aromatic -OH compounds (phenols) are much more soluble than the corresponding linear alcohols; the C₇ aliphatic alcohol *n*-heptanol has a solubility of 8×10^{-3} M, and the cresols (H₃C-Ph-OH) around 0.2 M.

As more OH groups are introduced into a molecule, its solubility characteristics depend to some extent on how well it fits into the framework of the structured component of water. It has been noted that the spacings between oxygen atoms of many very water-soluble compounds correspond rather closely to the first and second nearest-neighbor distances of the ice lattice (Berendsen, 1975). Seemingly minor changes in the stereochemistry of polyfunctional compounds often, however, lead to

changes in solubility that are not well understood. These differences have been studied for some cyclic polyols and monosaccharides. For example, the oxygen atoms of β -D-glucose (**17**), which are all equatorially disposed, fit very well into an ice lattice; the water-water hydrogen bonds of the lattice are replaced by glucose-water bonds, and the solubility of glucose is extremely high (90 g/100 mL H_2O); but mannose (**18**), in which the 3-OH is axial, has a solubility of 250 g/100 mL, and β -D-galactose (**19**), with a 5-axial OH, has a solubility of 58 g/100 mL (Tait et al., 1973).

Many naturally occurring substances as well as compounds of anthropogenic origin are amphiphilic; that is, contain a highly polar region and a nonpolar region. Fatty acids and synthetic detergents are straightforward examples of this class of compounds, but polymeric dissolved organic species such as humic substances (see Sections 1.B.1f and 1.B.3a) also display these characteristics (Wershaw, 1986; Yonebayashi and Hattori, 1987). At very low concentrations, these substances may exist in true solution, but as their concentrations increase, interactions among their hydrophobic portions become dominant, and they produce oligomeric aggregates which eventually form particles of colloidal dimensions, called micelles (Figure 1.7).

Figure 1.7. An idealized micelle, showing polar, hydrophilic head groups (circles) and hydrophobic chains (lines).

Humic macromolecules may not form true micelles, but because they appear to include distinct hydrophobic and hydrophilic regions (Wershaw, 1986), they might be classified as "self-micelles." As in the case of completely apolar solutes, the formation of micelles is favored by the reduced volume of water cavity space required to surround the micelle relative to its individual molecules, but in addition, the polar regions of amphiphiles are oriented at the surface of the micelle and provide additional solubilizing capacity through ionic interactions, especially if they are charged.

The aggregates of many surface-active compounds are capable of enhancing the solubility of nonpolar organic compounds by bringing them into association with the hydrophobic portion of the amphiphilic cluster (Kile and Chiou, 1989). Humic aggregates and micelles, in particular, may incorporate nonpolar materials such as hydrocarbons, a property that gives them the ability to act as soaps and detergents and transport hydrophobic substances into the aqueous phase (Carter and Suffet, 1982). In the environment, this property becomes important in spills of materials such as petroleum; some of the insoluble hydrocarbons can become incorporated into naturally occurring micelles. For example, dissolved organic matter from seawater was shown to enhance the solubility of *n*-alkanes, but not branched or aromatic hydrocarbons (Boehm and Quinn, 1973). Other investigators, however, have found that the solubility of aromatic hydrocarbons was increased by some samples of humic material (Gauthier et al., 1987); humic substances with higher aromatic carbon content were generally more efficient at binding pyrene. It is possible that dissolved organic matter may enhance solubility of some, especially aromatic, hydrocarbons and quinones by charge-transfer interactions (Kress and Ziehmman, 1977; Melcer et al., 1987). The solubilities of hydrophobic compounds such as chlorinated pesticides have also been reported by many investigators to be enhanced in the presence of humic and fulvic acids (see, e. g., Chiou et al., 1986), although the enhancements vary greatly, depending on the source and chemical characteristics of the humic material (Chiou et al., 1987).

Amphiphilic compounds are also surface-active; their differently polarized regions cause them to accumulate at interfacial zones in the environment. For example, at the air-water interface, amphiphiles tend to orient themselves in "surface microlayers" or "surface films" (see Section 1.B.2d), where the polar region of the molecule is associated with the water phase and the nonpolar region is forced out of solution and extends up into the air phase. Often these surface layers are visible by the damping effect they exert on wave action (Figure 1.8); they are apparent as smoother patches among the ripples on a lake or in the ocean.

b. Marine Waters and Estuaries

The oceans. The volume of water contained in the world's oceans (about 1.4×10^9 km³, or 1.4×10^{21} liters) defies the imagination. A generalized cross-section of the ocean (Figure 1.9) illustrates that only a small fraction of its water occurs near the surface; approximately half of it is more than 4 km deep. The range of hydrostatic pressure (1–1000 bars) in the seas is significant because at high pressures water no

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