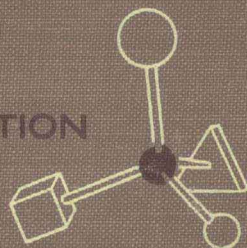


SECOND EDITION



ORGANIC CHEMISTRY

A BRIEF COURSE

BREWSTER AND McEWEN

ORGANIC CHEMISTRY

A BRIEF COURSE

by

Ray Q. Brewster

and

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The University of Kansas*

Second Edition

PRENTICE-HALL, INC.

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ORGANIC CHEMISTRY

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PREFACE TO SECOND EDITION

In preparing the revision of this textbook, we have rewritten and rearranged the material almost completely—in such a way that the properties of aliphatic and aromatic compounds are presented in an integrated manner. This unified treatment of the subject matter is advantageous in a course limited to one semester or two quarters, although a student may find the study of fundamental principles, as illustrated by the various classes of hydrocarbons, somewhat tedious before he begins consideration of other types of carbon compounds which, to him, are usually of greater significance. In order to gain the student's interest at the outset, the authors have devoted the first chapter to an introductory study of methyl and ethyl alcohols, whose simple transformations clearly reveal the important relationships existing among several prominent families of carbon compounds. Thereafter, the various classes of hydrocarbons and their derivatives are presented in logical order.

Throughout the book somewhat more stress has been laid upon mechanisms of reaction than is found in most texts designed for a short course. It is the authors' conviction that, even though but one semester or two quarters may be available for the study of organic chemistry, principles and theoretical topics should not be minimized to make room for a greater abundance of descriptive material. Both the observed facts and their interpretation are important. Hence, the electronic theory has been utilized throughout the text in the explanation of the properties of various classes of compounds. However, in order to avoid overwhelming the student at the start of the semester, the theoretical material is introduced in a gradual manner. For example, resonance and molecular orbital theory are introduced in simplified form in early chapters; the expansion and more rigorous treatment of these theoretical ideas are given later.

Illustrative material has been revised to include some of the newer processes and products. Many recent developments in biological and medicinal chemistry have been incorporated into appropriate chapters. Also, biographical and historical footnotes have been used to convey to the student some knowledge of the history of chemistry. At the conclusion of

each chapter new questions and problems have been added to those appearing in the first edition. Answers to problems are given in the appendix.

The senior author welcomes as his collaborator in this revision of the textbook Professor William E. McEwen to whom credit is due for much of the newer material.

RAY Q. BREWSTER
WILLIAM E. MCEWEN

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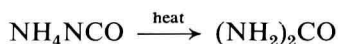
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Friedrich Wöhler¹

FOREWORD

1. The field of organic chemistry. Organic chemistry may be defined as the chemistry of the carbon compounds. Many such compounds are produced by living organisms, both plant and animal, and for many years it was supposed that carbon compounds, other than very simple ones such as carbon dioxide, could be obtained only by the aid of certain “vital forces” that the living cells must supply. The overthrow of this “vital force theory” was brought about during the first half of the nineteenth century by the production of several organic substances from nonliving sources. Among the first organic compounds to be produced by synthetic means was urea, an end product of the metabolism of protein and present in the urine of all mammals. This was obtained in 1828 by Wöhler when he noticed that the evaporation of a solution of ammonium cyanate converted a portion of this inorganic salt to urea. In retrospect, this experiment appears to provide a



synthesis of an organic compound from an inorganic one, but in 1828 all ammonia was obtained by heating animal refuse with lime and it could be argued that the “vital force” was still present. Now that synthetic ammonia,

¹ Friedrich Wöhler (1800–1882), German chemist, was for many years a professor of chemistry at Göttingen. He is noted for the discovery of aluminum (1827) as well as for his contributions to the chemistry of boron, silicon, and titanium. In the organic field he added much to the knowledge of isocyanates and carried out some pioneer work on the study of uric acid.

from the combination of nitrogen and hydrogen, is available in almost any desired quantity, the synthesis of urea is not only a scientific accomplishment of the research laboratory but actually a large commercial enterprise since, among other uses, urea serves as a nitrogen supplement in the feeding of cattle and as one reactant in the production of certain types of plastics. The old classifications of substances as organic or inorganic continue in use to the present day, but the original significance of the terms has long since disappeared.

Of course the understanding of the chemical processes necessary for such production of organic compounds was acquired very slowly, but, as the complexities of the structure of matter began to unfold, man's knowledge grew, like the snowball, with ever increasing speed. The methods of building molecules consisting of atoms of carbon, hydrogen, oxygen, and sometimes a few other elements, have now become so well developed that the term "creative chemistry" has acquired a very real meaning, and compounds can be built (synthesized) to meet exacting specifications. Thus, the chemical laboratory and its attendant manufacturing plant have, in many instances, become both co-workers with and rivals of nature.

The achievements of synthetic organic chemistry have been widely publicized, but it may be well to mention such attainments as the manufacture of synthetic rubber, plastics, textiles, dyes, medicinals, and numerous other types of compounds. Such materials, whether of natural occurrence or entirely man made, serve a wide variety of purposes and have the common property of containing carbon. Such carbon compounds comprise the field of organic chemistry.

The early chemists classified organic compounds into two broad divisions: (1) the "aliphatic" series, comprising the fats (tallow, olive oil, and so forth) and compounds related to them, and (2) the "aromatic" series, consisting of the essential oils of plants, such as oil of wintergreen, oil of geranium, and other flavoring principles. The names "aliphatic" and "aromatic" are still retained for the two chief divisions of organic compounds, but the fatty character or the aroma of a compound has long since ceased to be the basis of its classification. We shall see that the carbon atoms of aliphatic compounds are connected in chains and that the aromatic compounds are characterized by a certain type of cyclic structure.

2. Review of atomic structure and atomic linkages. Before beginning a discussion of the structure of organic compounds, it may be well to remind the student of the principles of atomic structure and valence that were studied in his earlier courses in inorganic chemistry. It will be recalled that the three ultimate particles with which we are concerned in discussing atomic structure are protons, neutrons, and electrons. The positive charge upon the nucleus of an atom is determined by the number of protons in it. This positive charge is exactly balanced by the negative charge on an equal number of electrons

arranged around the nucleus. The neutrons are associated with the protons in the nucleus but have no charge and contribute only mass to the atom.

The structures of a few of the simplest atoms are illustrated by the diagrams in figure 1 below. The innermost shell of electrons (called the K shell) consists of two electrons in all atoms beyond hydrogen, and the next shell (L shell) may not exceed eight electrons. The third layer (M shell) may have as many as eighteen electrons in some of the heavier elements; but, for the elements of the second period of the periodic table, where the M shell is outermost, it also has a maximum of eight electrons. In the rare gases, helium, neon, and argon, it will be noticed that each of the electron shells is completely filled. Such an electronic arrangement has a maximum of stability

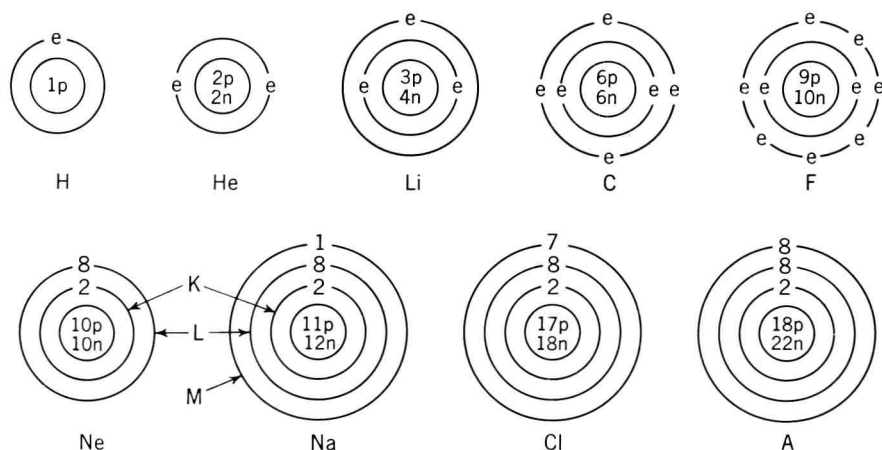


Fig. 1. Atomic structure.

so that the rare gases are chemically inert; that is, they have little tendency to lose or gain electrons by reaction with other elements or even to share their electrons with other atoms. Chemical reactions of the elements are determined by the number of electrons in the outer layer (valence shell) of their atoms, and the atoms of the elements may transfer electrons from one to another (electrovalence) or share electrons between two elements (covalence) in order to obtain a stable arrangement.

2.1 The electrovalent bond. It will be observed from the following diagrams that the loss of the outermost electron from a lithium atom leaves a positive lithium ion whose outer shell has two electrons as in the inert helium atom. The gain of this electron by a fluorine atom produces a negative fluoride ion in which the outer shell has eight electrons as in the neon atom. By becoming ions the lithium and fluorine atoms have attained maximum stability, and the lithium and fluoride ions are held together in the crystal lattice in lithium fluoride by their opposite electrical charges.

A similar transfer of the outermost electron in a sodium atom to a chlorine atom produces sodium and chloride ions, in each of which there are eight electrons (a complete octet) in the outer shell. The sodium and chloride ions, consequently, have the same outer electronic structures as the inert gases, neon and argon, respectively. Such a transfer of one or more electrons from one atom to another results in an "electrovalent bond" (or "ionic bond"). Electrovalent compounds are generally characterized by having high melting points and high boiling points, forming ionic crystal lattices, and producing solutions in ionizing solvents that are good conductors of electricity.

2.2 The covalent bond. In such compounds as methane, carbon tetrachloride, and methyl alcohol, electrons are shared between two atoms as

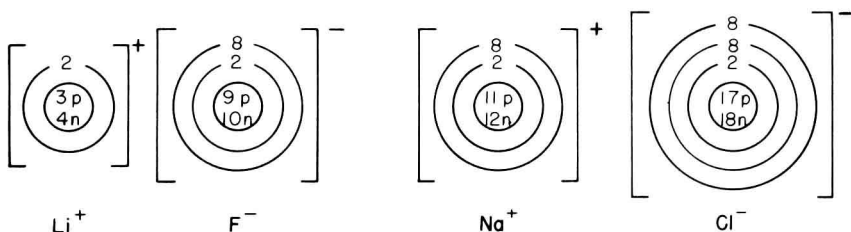
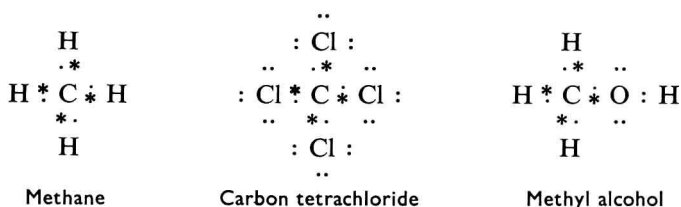


Fig. 2. Electrovalent compounds.

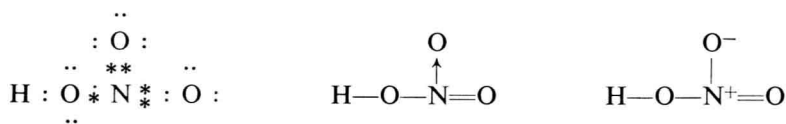
illustrated by the following formulas. Electrons of the carbon atoms are represented by asterisks; and electrons of other elements by dots.² Only electrons of the outer (valence) shell are shown.



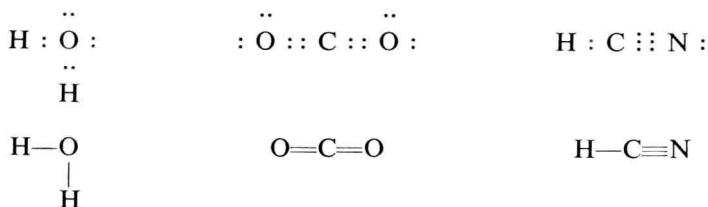
In these compounds no transfer of electrons from one atom to another occurs, but the carbon, chlorine, and oxygen atoms each have eight electrons in their outer shells by sharing electrons between them. Hydrogen is held to the carbon or oxygen by a shared pair of electrons. Such sharing of electrons between atoms forms a "covalence." As compared with electrovalent compounds, substances containing covalences generally have low melting points, low boiling points, and their water solutions are nonconductors of electricity.

² It is understood, of course, that an electron of an atom of one element is exactly like an electron of an atom of another element. The use of different symbols, therefore, is not exactly logical but is convenient for clarity of expression.

2.3 The coordinate covalent bond. In a typical covalent compound, such as carbon tetrachloride, each of the two connected atoms contributes one of the electrons of the shared pair. In other instances, both of the shared electrons may be supplied by only one of the atoms. Such a type of bond is known as a “coordinate covalence” and may be illustrated with nitric acid. The nitrogen electrons are represented by asterisks, and electrons of the other elements by dots. Hydrogen has one electron; oxygen, six; and nitrogen, five in their valence shells. The formula shown below provides a shared pair of electrons for the hydrogen atom and an octet (four shared pairs) for the other elements. It should be emphasized once again that nitrogen and oxygen can accommodate but eight electrons in their valence shells, and cognizance must be taken of this fact in the writing of any structural formula for molecules containing these elements. In the structural formula for nitric acid shown below, one of the oxygen atoms is held to the nitrogen by sharing a pair of electrons, which is provided entirely by the nitrogen atom. It may be considered that, in a formal sense, the nitrogen has given one of its electrons to the oxygen in order that the oxygen may have an electron to pair with another electron from the nitrogen atom. Hence, the oxygen has acquired a negative charge by gaining an electron; and the nitrogen, a positive charge by the corresponding loss of an electron. Such a coordinate covalent bond is often indicated by an arrow or by placing a formal positive charge on the donor atom (nitrogen in this example) and a negative charge on the acceptor atom (oxygen). The type of covalent bond in which each atom supplies one electron of the shared pair is indicated by a dash. It is also worthy of comment that the theory of resonance (page 64) modifies our concept of the structure of nitric acid and similar molecules in a way that will be described later.



3. Single, double, and triple covalent bonds. Covalent bonds may be formed by sharing one, two, or three pairs of electrons. Bonds of these types may be illustrated by water, carbon dioxide, and hydrocyanic acid, respectively.



The upper row of formulas shows the sharing of electrons and the lower row of graphic formulas indicates the three types of bonds by single, double, and