

---

# ORGANIC CHEMISTRY

## AN INTERMEDIATE TEXT

---

SECOND EDITION

Robert V. Hoffman

New Mexico State University



A JOHN WILEY & SONS, INC., PUBLICATION



# ORGANIC CHEMISTRY

SECOND EDITION



---

# ORGANIC CHEMISTRY

## AN INTERMEDIATE TEXT

---

SECOND EDITION

Robert V. Hoffman

New Mexico State University



A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2004 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.  
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-750-4470, or on the web at [www.copyright.com](http://www.copyright.com). Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, e-mail: [permreq@wiley.com](mailto:permreq@wiley.com).

**Limit of Liability/Disclaimer of Warranty:** While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

***Library of Congress Cataloging-in-Publication Data***

Hoffman, Robert V.

Organic chemistry : an intermediate text / Robert V. Hoffman.—2nd ed.  
p. cm.

Includes bibliographical references and index.

ISBN 0-471-45024-3 (cloth)

1. Chemistry, Organic. I. Title.

QD251.2.H58 2004

547—dc22

2004014949

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

To Rose





---

# CONTENTS

---

<b>Preface</b>	<b>xiii</b>
<b>Preface to the First Edition</b>	<b>xv</b>
<b>1 Functional Groups and Chemical Bonding</b>	<b>1</b>
Functional Groups / 1	
Orbitals / 5	
Bonding Schemes / 7	
Antibonding Orbitals / 13	
Resonance / 18	
Conjugated $\pi$ Systems / 21	
Aromaticity / 23	
Bibliography / 26	
Problems / 27	
<b>2 Oxidation States of Organic Compounds</b>	<b>32</b>
Oxidation Levels / 32	
Oxidation States in Alkanes / 34	
Oxidation States in Alkenes / 34	
Oxidation States in Common Functional Groups / 35	
Oxidation Level Changes During Reactions / 35	
Bibliography / 41	
Problems / 41	
<b>3 Acidity and Basicity</b>	<b>47</b>
Bronsted and Lewis Acids and Bases / 47	
Acid Strength / 49	
Acid–Base Equilibria / 53	

Amphoteric Compounds / 56  
Structural Effects on Acidity / 56  
    Electronegativity / 58  
    Inductive Effects / 59  
    Resonance Effects / 61  
Bibliography / 63  
Problems / 63

**4 Curved-Arrow Notation** **69**

Electron Movement / 69  
Heterolytic Bond Cleavages / 70  
Heterolytic Bond Formation / 71  
Homolytic Bond Making and Bond Breaking / 73  
Resonance Structures / 75  
Depiction of Mechanism / 76  
Bibliography / 82  
Problems / 82

**5 Mechanisms of Organic Reactions** **86**

Activation Energy / 87  
Activated Complex / 88  
Reaction Energetics / 89  
Structure of the Activated Complex / 91  
Hammond Postulate / 96  
Reaction Kinetics / 99  
Determining Activation Energies / 104  
Isotope Effects / 105  
Electronic Effects / 110  
Hammett Equation / 111  
Bibliography / 118  
Problems / 118

**6 Stereochemical and Conformational Isomerism** **124**

Stereochemical Structures / 125  
Chirality / 128  
Configuration of Chiral Centers / 129  
Multiple Stereocenters / 132  
Optical Activity / 137  
Absolute Configuration / 138  
Physical Properties of Enantiomers / 139  
Resolution of Enantiomers / 140  
Stereoselective Reactions / 144

Formation of Enantiomers /	144
Formation of Diastereomers /	146
Stereochemistry to Deduce Mechanism /	152
Conformational Analysis /	157
Conformational Energies /	164
A Values /	166
Strain in Ring Systems /	167
Stereoelectronic Effects /	172
Bibliography /	176
Problems /	176

## **7 Functional Group Synthesis** **183**

Functional Group Manipulation /	183
Carboxylic Acids /	185
Esters /	188
Amides /	190
Acid Chlorides /	191
Aldehydes /	192
Ketones /	194
Imines and Imine Derivatives /	197
Alcohols /	198
Amines /	201
Alkenes /	203
Alkanes /	207
Bibliography /	208
Problems /	209

## **8 Carbon–Carbon Bond Formation between Carbon Nucleophiles and Carbon Electrophiles** **216**

Synthetic Strategy /	217
Nucleophilic Carbon /	218
Electrophilic Carbon /	220
Reactivity Matching /	223
Generation of Nucleophilic Carbon Reagents /	224
Generation of Electrophilic Carbon Reagents /	227
Matching Nucleophiles with Electrophiles /	227
Enolates /	228
Enolate Regioisomers /	234
Diastereoselection in Aldol Reactions /	236
Organometallic Compounds /	239
Neutral Carbon Nucleophiles /	239
C=C Formation /	242
Cyclopropanation Reactions /	244

Metal-Catalyzed Carbon–Carbon Bond Formation / 246  
Pd(0)-Catalyzed Carbon–Carbon Bond Formation / 247  
    Heck Reaction / 251  
    Suzuki Coupling / 253  
    Stille Coupling / 254  
Olefin Metathesis / 256  
Bibliography / 261  
Problems / 262

**9 Carbon–Carbon Bond Formation by Free-Radical Reactions** **272**

Free-Radical Reactions / 272  
Free-Radical Polymerization / 277  
Nonpolymerization Reactions / 278  
Free-Radical Initiation / 280  
Free-Radical Cyclization / 283  
Bibliography / 288  
Problems / 288

**10 Planning Organic Syntheses** **292**

Retrosynthetic Analysis / 292  
Carbon Skeleton Synthesis / 296  
Umpolung Synthons / 302  
Acetylide Nucleophiles / 305  
Ring Construction / 306  
Robinson Annulation / 310  
Diels–Alder Reaction / 312  
HOMO–LUMO Interactions / 313  
Stereoelectronic Factors / 316  
1,3-Dipolar Cycloadditions / 319  
Bibliography / 323  
Problems / 324

**11 Structure Determination of Organic Compounds** **332**

Structure Determination / 332  
Chromatographic Purification / 333  
Instrumental Methods / 335  
Nuclear Magnetic Resonance / 336  
Chemical Shift / 338  
Spin–Spin Coupling / 344  
Descriptions of Spin Systems / 350

Second-Order Splitting /	354
Structure Identification by $^1\text{H}$ NMR /	355
Carbon-13 NMR /	360
Infrared Spectroscopy /	366
IR Stretching Frequencies /	367
Use of IR Spectroscopy for Structure Determination /	371
Mass Spectrometry /	377
Fragmentation Processes /	384
Bibliography /	388
Problems /	388
<b>Solutions to Chapter Problems</b>	<b>395</b>
<b>Index</b>	<b>471</b>



---

# PREFACE

---

In keeping with a mechanistic emphasis, the book was reorganized. The chapter on mechanism is now Chapter 5 instead of Chapter 10. Thus the first six chapters focus on the mechanistic and structural underpinnings of organic chemistry. Synthetic aspects of organic chemistry are then discussed from a mechanistic and structural point of view. Several new sections have been added and others expanded. An expanded discussion of resonance and aromaticity is found in Chapter 1. A section on organopalladium chemistry and olefin metathesis has been added to Chapter 8 as they relate to current methods of carbon–carbon bond formation. Chapter 9 on free-radical reactions for carbon–carbon bond formation has been revised. The discussion of Diels–Alder chemistry has been moved to Chapter 10 and expanded. A number of new problems have been added which serve to further illustrate the principles developed in each chapter. Finally, thanks to input from many people who have read this text and taught from it, the discussion has been further honed and errors corrected.

What has evolved is a greater initial emphasis of the mechanistic and structural approach to organic chemistry. The application of these principles in a discussion of modern synthetic methodology (functional group manipulation, carbon–carbon bond formation, retrosynthetic analysis) provides a new organizational framework for understanding many of the most common and most important synthetic reactions.

What has not changed is the premise that this text is meant to provide the tools students need to master the material in advanced courses or compete successfully in the workplace.

ROBERT V. HOFFMAN





---

# PREFACE TO THE FIRST EDITION

---

This text was inspired by two observations. The first is that many entering graduate students took organic chemistry as sophomores but since that time have had little exposure to organic chemistry in a formal sense. Because of this time lapse in their organic preparation, they often have difficulty performing well when placed directly into mainstream graduate level organic courses. What is much more effective is to first place them in a course which will bring them back up to speed in basic organic chemistry and at the same time introduce many of the advanced topics which are crucial to understanding current advances in the field. A course well suited for this purpose is a one-semester, advanced organic course at the senior undergraduate/beginning graduate level. Most departments, including ours, have such a course in place. Textbook selection for this course is problematic, however. If one of the standard advanced texts is used, only a small part is actually covered and students are not prepared to master the complexities, whereas if an undergraduate text is used, it often fails to push the students to the next level. Consequently, there is a real need for a one-semester text which gives a review of basic principles in addition to an exposure to the ideas which are currently of great importance in organic chemistry. This text was written to fill this need.

A second observation instrumental in shaping the approach of this text was made during group discussions of the organic faculty and students. One common exercise is to present practice cumulative exam problems to the group and discuss ways in which they might be solved. It is very common for the students to analyze the question in terms of reactions and transformations and try to arrive at a solution based on the question as written. On the other hand, it is very common for the faculty to ask very simple questions first—for example, “What is the oxidation change?” “What is the  $pK_a$  of the acid and what is the base?” and “What stereochemical changes occur?” It is clear that more experienced organic chemists begin from a very basic point of view and progress to a more complex solution, whereas novice organic chemists tend to jump in at a much more difficult level. It thus appears very important to initially emphasize the basic principles on which organic chemistry depends and then progress to more specialized topics, all the while emphasizing their relationship to the basic principles. This text utilizes this organizational approach.

The result is a textbook designed for a one-semester advanced organic chemistry course. First and foremost it is a textbook and not a reference text. There is plenty of material to fill a semester, but it is not comprehensive in its coverage. Topics were chosen to provide a basic and well-rounded discussion of ideas important in modern organic chemistry and to provide students with the necessary tools to succeed in more specialized advanced courses. It is a book to be taught from; thus instructors should take the opportunity to include special or favorite topics at appropriate points. References to alternative textbook and literature reviews of the subjects are included so that students can go to the library and get a different explanation. This is important for encouraging students to do library work as a means to independently gain insight and understanding. Finally, there are abundant problems included at the end of each chapter so that students can practice applying what they are learning. Working problems is the single most effective way to learn and organize the large amount of information that is encountered in organic chemistry, so there are a large number of practice problems available at all levels of difficulty.

The goal of this text is to provide senior undergraduate students the organic background required to move on successfully in their careers. For beginning graduate students lacking this background, it provides a succinct yet rigorous preparation for advanced organic courses.

R.V.H.

## FUNCTIONAL GROUPS AND CHEMICAL BONDING

---

Functional Groups	1
Orbitals	5
Bonding Schemes	7
Antibonding Orbitals	13
Resonance	18
Conjugated $\pi$ Systems	21
Aromaticity	23
Bibliography	26
Problems	27

### FUNCTIONAL GROUPS

There are over 12 million known compounds of which more than 80% are organic compounds. To make sense out of the nearly 9 million organic compounds and be able to manipulate them and make new compounds, there must be some system of organization whereby organic compounds can be categorized by a particular property or group of properties. A natural method utilized by early practitioners was to group organic compounds by the reactions that they underwent. Thus there developed a whole variety of qualitative tests called classification tests which

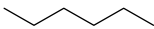

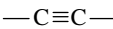
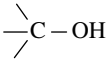


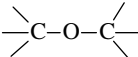












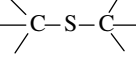
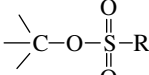
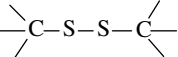
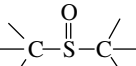
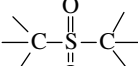


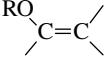
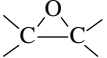
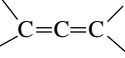
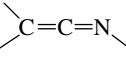
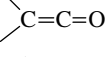
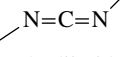
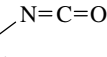
could be used to systematically categorize the reactivity of a compound and thus allow it to be grouped with others of similar chemical reactivity. These tests are still very useful to practicing organic chemists and collectively are known as organic qualitative analysis.

Classification tests are used to distinguish organic compounds and segregate them into different functional classes based on their chemical properties. Originally a group of compounds that showed similar chemical behavior based on the classification tests were named for a property or behavior (e.g., acids from *acer* meaning “sour,” aromatic compounds from their odors). With the evolution of the science of chemistry and the development of more modern views of atoms and molecules, a different definition of functional classes is possible. The behavior of organic compounds is now organized into patterns that are based on recurrent groups of atoms—functional groups. The sites in molecules at which chemical reactions occur are localized at the functional groups in the molecule; the rest of the molecule is the same after the reaction as before. Thus, instead of thinking of the whole molecule in terms of its chemical reactivity, it is only necessary to recognize what functional group or groups are present in the molecule. It is then possible to predict the chemical behavior of the molecule based on the known chemistry of the functional groups that it contains.

This turns out to be a huge simplification. Since the numbers of functional groups are relatively small, it is possible to classify a very large number of individual compounds by a relatively small number of functional groups. So the first step to enlightenment in organic chemistry is to realize the key role that functional groups play in simplifying the subject, and the second step is to learn the functional groups by name, structure, and formula. While a great number of them may have already been encountered in the introductory organic course, it is helpful to review them. Table 1.1 is a list of the most common functional groups. While there are quite a few other functional groups that are not shown, those found in Table 1.1 are the most common and are present in the vast majority of organic compounds. Notice that not all functional groups contain only carbon atoms (e.g., the nitro group and the carbodiimide groups), and some functional groups differ at atoms other than carbon (compare the nitro and nitroso groups and the sulfoxide and sulfone groups). Since functional groups are reference points for predicting and understanding the reactions of individual organic molecules, it is very important to be able to recognize these functional groups (and others that might be encountered in the future). It is also useful to learn normal structural abbreviations that are used to indicate functional groups that are present in chemical structures. The abbreviations in Table 1.2 correspond to the groups that are shown in Table 1.1.

A major reason that the behavior of organic compounds can be generalized in terms of the functional groups they contain is because the bonds holding a given functional group together are the same regardless of the compound which contains that functional group. The four compounds shown below all contain the carboxylic acid functional group, which is highlighted within the boxes. Thus all

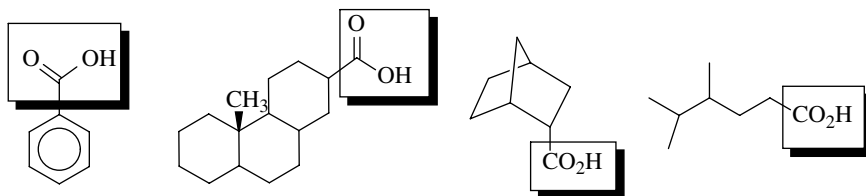
Table 1.1 Common Functional Groups

		
alkane	alkene	alkyne
		
alcohol (1°, 2°, 3°)	aldehyde	carboxylic acid
		
ether	ketone	ester
		
amine (1°, 2°, 3°)	aldimine	amide (1°, 2°, 3°)
		
alkyl halide (1°, 2°, 3°)	ketimine	nitrile
		
nitroso	nitro compound	acid chloride
		
mercaptan, thiol	sulfide	sulfonate ester
		
disulfide	sulfoxide	sulfone
		
acetal	aromatic	enol ether
		
epoxide	allene	keteneimine
		
ketene	carbodiimide	isocyanate

**Table 1.2 Common Functional Group Abbreviations**

Alkane	R
Alkene	$R_2C=CR_2$
Alkyne	$RC\equiv CR$
Alcohol	ROH
Aldehyde	RCHO
Carboxylic acid	$RCO_2H$
Ether	ROR
Ketone	$RC(O)R$
Ester	$RCO_2R$
Amine	$RNH_2, R_2NH, R_3N$
Aldimine	$RHC=NR$
Amide	$RC(O)NH_2, RC(O)NHR, RC(O)NR_2$
Alkyl halide	RX
Ketimine	$R_2C=NR$
Nitrile	RCN
Nitroso	RNO
Nitro	$RNO_2$
Acid chloride	$RC(O)Cl$
Mercaptan, thiol	RSH
Sulfide	RSR
Sulfonate ester	$RSO_3R'$
Disulfide	RSSR
Sulfoxide	$RS(O)R$
Sulfone	$RSO_2R$
Acetal	$(RO)_2CR_2$
Aromatic	Ar-X
Enol ether	$ROCH=CR_2$
Allene	$R_2C=C=CR_2$
Ketene	$R_2C=C=O$
Keteneimine	$R_2C=C=NR$
Carbodiimide	$RN=C=NR$
Isocyanate	RNCO

four contain the bonding pattern characteristic of the  $-COOH$  functional group which is *independent of the bonds found in rest of the molecule!*



Since most organic reactions involve the conversion of one functional group to another, it follows that most organic reactions quite simply involve bond

changes involving functional groups. If one knows the bonds found in the reactant functional group and the bonds found in the product functional group, then one automatically knows what bonding changes are required to effect the desired chemical change. Thus, in addition to being able to recognize functional groups, it is also important to be able to describe the numbers and types of bonds found in functional groups.

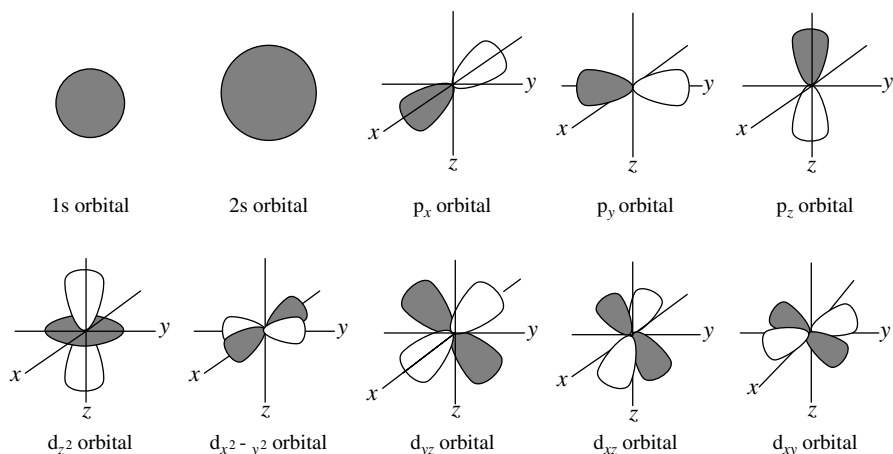
Bonds in functional groups can first be described by Lewis structures, which are merely formalisms for denoting numbers of shared and unshared electron pairs, formal charges, and types of bonds (numbers of shared pairs, single, double, and triple). Chemistry students learn to write Lewis structures in virtually all of their early chemistry courses. How to write Lewis structures will not be reviewed here, but knowing the correct Lewis structures for molecules and functional groups in molecules is an indispensable first step in being able to describe the structure and bonding of functional groups.

The next level of insight into functional groups comes from the translation of Lewis structures into more accurate bonding descriptions based on modern bonding theories. Structural details including geometries also result from the proper description of the bonding in the functional group. The ideas of structure and bonding currently in use had their origins in the late 1920s. It is again beyond the scope of this book to trace the developments which were seminal in the development of current theories; however, early studies were all rooted in the quest to understand and be able to describe the behavior of electrons in atoms. The development of quantum mechanics and the particle–wave duality of the electron and the uncertainty principle led to mathematical descriptions of the behavior of electrons in the electric field of the nucleus. The solution of those equations resulted in a new conceptual framework for understanding chemical bonding.

## ORBITALS

The theory suggests that the behavior of each electron in an atom can be described by a wave function ( $\psi$ ), which is a function of the space coordinates of the electron and thus has spatial characteristics. These one electron wave functions are called atomic orbitals (AOs). Atomic orbitals describe electron densities in the atom at various distances and directions from the nucleus. By choosing a low constant absolute value for the wave function, a contour surface can be constructed. The probability of finding an electron ( $\psi^2$ ) is highest inside the contour surface.

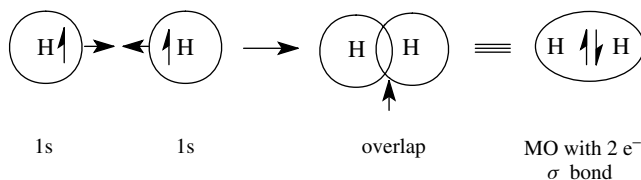
Thus instead of thinking of where an electron *is*, it is more correct to think about where the electron is *likely to be*. Orbitals are thus regions of space where an electron is more likely to be found. These regions of space, which have a significant electron population (orbitals), have shape, size (distance from the nucleus), and energy. Familiar examples of s, p, and d AOs are shown in Figure 1.1. The most common elements present in organic compounds are first-row elements (C, H, N, O); therefore 1s, 2s, and 2p AOs are most commonly encountered. The concept of AOs was a breakthrough in understanding the properties of atoms.



**Figure 1.1** Depiction of s, p, and d atomic orbitals.

In molecules, the problem of understanding the interactions of electrons with the nuclei is more complicated because there are more nuclei and more electrons that interact. Imagine, however, the situation that occurs when two nuclei approach one another. If the two atoms come close enough together, an AO of one atom which contains a single electron will occupy to some extent *the same* region of space as an AO of the second atom which contains a single electron. When those AOs overlap, an electron from one atom shares a region of space with the electron from the other atom. When such an event occurs, each electron is no longer influenced by just one nucleus but by two. This requires a new mathematical description of the behavior of electrons influenced by two nuclei. Again the solution to those equations defines a new region of space where there is a high probability of finding *both* electrons. Furthermore, only two electrons can occupy any particular region of space. This new region of space is called a molecular orbital (MO), the electrons in the MO are of lower energy than when they were in their separate AOs, and the lowered energy gives rise to a chemical bond between the atoms. This process is shown in Figure 1.2.

In other words, chemical bonds result from the overlap of singly occupied AOs to give a doubly occupied MO (called a bonding MO) in which each electron of the pair interacts with both nuclei. Because each of the electrons interacts



**Figure 1.2** Cartoon version of the overlap of 1s atomic orbitals to give a new bonding molecular orbital.

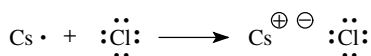


with two nuclei, they are more tightly bound (i.e., they are of lower energy) than they were in the separated atoms and are more likely to be found between the two nuclei.

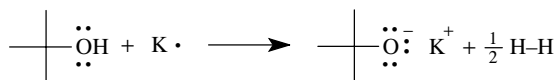
Because the total number of interacting orbitals is conserved, the interaction of two AOs gives rise not only to the bonding MO of lower energy but also to an MO of higher energy called an antibonding MO. This orbital is normally unfilled by electrons; however, it can play a role in chemical reactions. For now we will concentrate on bonding MOs formed by the overlap of atomic orbitals.

## BONDING SCHEMES

Bond formation between atoms occurs primarily to enable each atom to achieve an inert gas electron configuration in the valence level (a valence octet for all elements except hydrogen which requires only two electrons to achieve the electronic configuration of helium). An atom can achieve an inert-gas electronic configuration by giving up electrons, accepting electrons, or sharing electrons with another atom. An ionic bond is formed when one atom gives up one or more electrons to reach an octet electronic configuration (as a positively charged ion) and a second atom accepts one or more electrons to reach an octet electronic configuration (as a negatively charged ion). For example, the reaction of a cesium atom with a fluorine atom occurs by the transfer of an electron from the cesium atom to the chlorine atom. By doing so, both cesium and chlorine have reached a valence octet electron configuration. The cesium atom has been converted to a positively charged cesium ion with the octet electronic configuration of xenon, and the chlorine has been converted to a negatively charged chloride ion with the octet electronic configuration of argon. The “bond” between cesium and chlorine is due to the electrostatic attraction of the cesium and chloride ions.

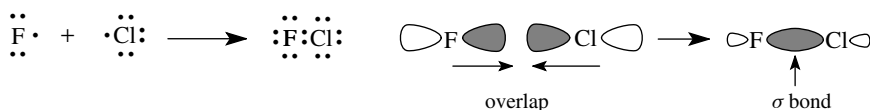


The reaction of potassium metal with *tert*-butanol gives an ionic bond between the *tert*-butoxy anion and a potassium cation by transfer of electrons from potassium to the hydroxyl functional group. Hydrogen is evolved as a by-product. By losing an electron, potassium gains the octet electronic configuration of argon, oxygen has an octet structure (three lone pairs and one pair of shared electrons), and hydrogen has the electronic configuration of helium. (Based on functional group behavior, any other alcohol is predicted to react with potassium in the same way—and they do!)



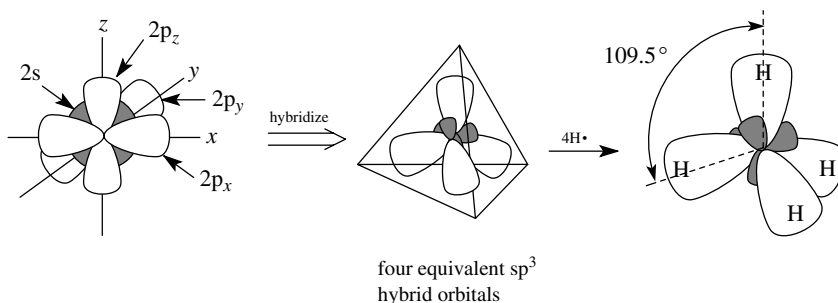
Most bonds in organic molecules, however, are covalent bonds in which electrons are shared between two atoms. Sharing electrons is a way to enable each

atom of the bonded pair to reach an octet electronic configuration without having to give up or gain an electron. Covalent bonds are formed by the overlap of singly occupied AOs to form new MOs that contain a pair of electrons. Each atom in essence gains an electron by sharing. The reaction of a chlorine atom with a fluorine atom occurs by the overlap of a singly occupied 3p orbital of chlorine with a singly occupied 2p orbital of fluorine to give a bond between the two atoms that contains two electrons. This is shown both by using Lewis structures and by using orbital pictures. The type of bond formed is called a  $\sigma$  bond because the region of greatest electron density falls on the internuclear axis.

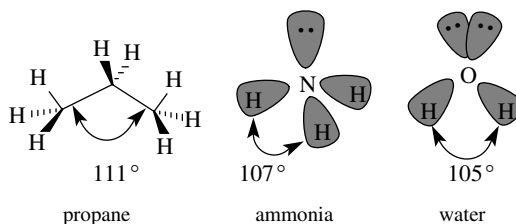


This simple picture is adequate for many diatomic molecules with univalent atoms, but it is not sufficient to describe the bonding in most polyatomic molecules. In addition to electron sharing to reach octet electronic configurations, other considerations such as the number of bonds to an atom, the number of electron pairs that are shared between two bonded atoms, and repulsion energies that are present between electron pairs require some modification of the picture. These factors can be rationalized by the idea that valence shell atomic orbitals (2s and 2p's) can combine to form hybrid AOs. These hybrid AOs overlap with AOs of other atoms in the usual fashion to form covalent bonds. Hybrid AOs have energies, shapes, and geometries which are intermediate between the atomic orbitals from which they are formed. Hybridization of AOs is an outgrowth of bond formation that enables atoms to derive the greatest amount of bond energy from electron sharing and to allow bonded atoms to achieve octet electronic configurations.

If four single bonds and/or electron pairs originate from a single atom, then the s orbital and the three p orbitals of the valence shell combine to form four equivalent  $sp^3$  hybrid orbitals that are then used in bond formation to other atoms. Depending on the number of electrons in the valence shell of the atom, these  $sp^3$  hybrid orbitals can contain either a single unpaired electron which can be shared with another atom by overlap and bond formation or an unshared pair of electrons which is normally not involved in bond formation. Thus alkanes, which have all single bonds, have carbon atoms which are  $sp^3$  hybridized. For example, methane has four single C–H bonds originating at carbon, and these bonds are  $\sigma$  bonds produced by the overlap of four  $sp^3$  hybrid orbitals of carbon with four 1s AOs of four hydrogens to give four  $sp^3$ –1s  $\sigma$  bonds from carbon to hydrogen. The geometry of the four equivalent  $sp^3$  hybrid orbitals (and hence the compound produced by overlap with these orbitals) is tetrahedral. Thus methane has four equivalent C–H  $\sigma$  bonds which point toward the corners of a regular tetrahedron and have H–C–H bond angles of  $109.5^\circ$ :



In a similar fashion each carbon of propane is  $sp^3$  hybridized and tetrahedral since each carbon has four single bonds to other atoms originating from it. For example, the central carbon of propane has two equivalent  $sp^3-1s$  C-H  $\sigma$  bonds and two equivalent  $sp^3-sp^3$  C-C  $\sigma$  bonds. (Note that  $sp^3$  orbitals from one carbon can overlap with  $sp^3$  orbitals from another carbon to produce carbon-carbon bonds.) The geometry is very close to tetrahedral, but the C-C-C bond angle is slightly larger ( $111^\circ$ ) to accommodate the bigger  $CH_3$  groups.

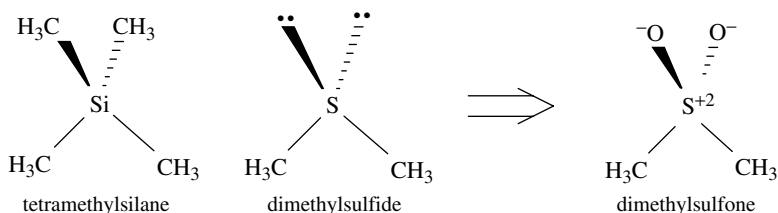


Other first-row elements can also be  $sp^3$  hybridized. The only requirement is that they have a combination of four single bonds and/or electron pairs originating from a single element. Ammonia, which has three N-H bonds and a lone pair on nitrogen, is thus  $sp^3$  hybridized and has three equivalent  $sp^3-1s$  N-H  $\sigma$  bonds and a lone pair which occupies an  $sp^3$  hybrid orbital. The geometry is close to tetrahedral with an H-N-H bond angle of  $107^\circ$ . Other amines also have  $sp^3$ -hybridized nitrogen and are close to a tetrahedral geometry around the nitrogen atom.

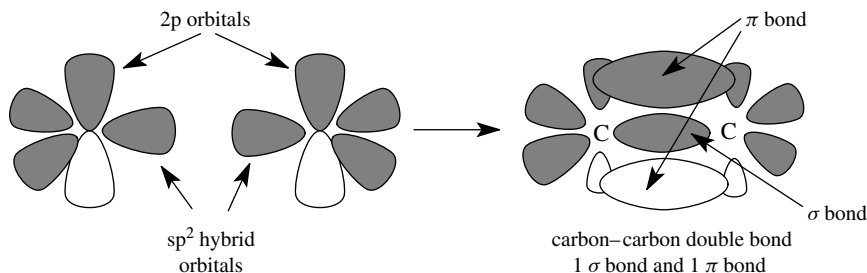
The oxygen atom in the water molecule has two bonds and two lone pairs so it too is  $sp^3$  hybridized. There are two equivalent  $sp^3-1s$  O-H  $\sigma$  bonds and two lone pairs occupying  $sp^3$ -hybridized orbitals. Electron-electron repulsions of the lone pairs cause greater distortions from a true tetrahedral geometry so that the H-O-H bond angle is  $105^\circ$ . Other singly bonded oxygen functional groups such as alcohols, ethers, and acetals have  $sp^3$ -hybridized oxygens and nearly tetrahedral geometries.

Second-row elements such as silicon, phosphorus, and sulfur can also have  $sp^3$  hybridization of the valence shell orbitals, although hybridization is not necessarily required for second-row elements. When second-row elements do hybridize,

however, the 3s and 3p AOs combine to form the  $sp^3$  hybrid orbitals. Tetramethylsilane, the standard reference for nuclear magnetic resonance (NMR) spectra, has tetrahedral geometry and thus  $sp^3$  hybridization of the 3s and 3p valence shell orbitals of silicon. Dimethyl sulfide has nearly tetrahedral bond angles, indicating that the sulfur is  $sp^3$  hybridized. Although formal charges are present, the two bonds to oxygen can be thought to arise by the overlap of a filled  $sp^3$  orbital on sulfur with an unfilled  $sp^3$  orbital on oxygen. The resulting  $\sigma$  bond is called a coordinate covalent, or dative, bond because both of the shared electrons in the bond come from only one of the bonded elements. Hydrogen sulfide has an H–S–H bond angle of  $92^\circ$ , which indicates that sulfur is not hybridized in this compound.



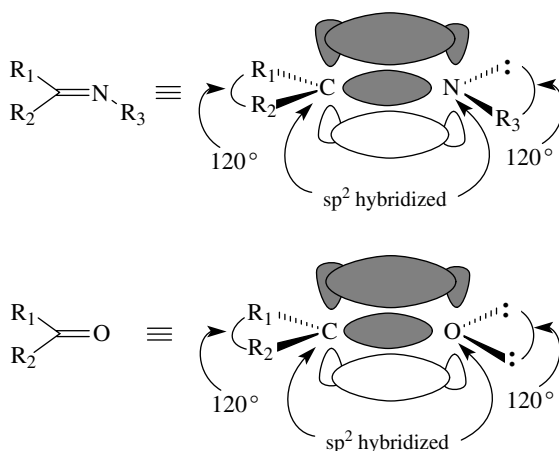
When two pairs of electrons are shared between two elements, a different bonding arrangement is required to enable the atoms to reach valence octet electron configurations. Because of the Pauli exclusion principle, only one sigma bond is possible between any two atoms because only one pair of electrons can occupy the space along the internuclear axis. The second pair of electrons that is shared by the two atoms must therefore be located in space someplace other than along the internuclear axis. The second pair of shared electrons is located in a different type of covalent bond, a  $\pi$  bond, which has electron density found on either side of the internuclear axis. The  $\pi$  bonding results from the parallel overlap (or sideways overlap) of atomic p orbitals. To accommodate the need for a singly occupied atomic p orbital available for the formation of a  $\pi$  bond, hybridization of the valence AOs takes place between the s orbital and two of the three p atomic orbitals. Hybridization of one s and two p AOs produces



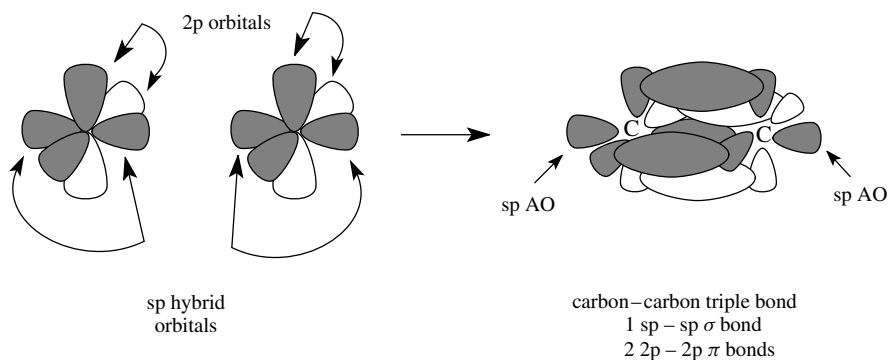
three equivalent  $sp^2$  hybrid AOs and a p orbital remains unhybridized in order to produce a  $\pi$  bond.

This bonding scheme permits two pairs of electrons to be shared between two atoms so that each pair occupies a different region of space and does not violate the Pauli exclusion principle. Since only two p orbitals are used in the hybridization and they are orthogonal and define a plane, the  $sp^2$ -hybridized carbon is planar with bond angles of  $120^\circ$ . The remaining p orbital, which is left unhybridized to form the  $\pi$  bond, is perpendicular to the molecular plane. Once formed, the  $\pi$  bond keeps the entire system rigid and planar, because rotation of one end of the  $\pi$ -bonded system relative to the other end requires that the  $\pi$  bond be broken.

Elements other than carbon are also  $sp^2$  hybridized if they share two electron pairs with another atom. Thus imines have  $sp^2$ -hybridized nitrogen (and carbon) to account for formation of the C–N double bond. The lone pair on nitrogen occupies an  $sp^2$  hybrid orbital. The bond angles are all  $120^\circ$  around both carbon and nitrogen since both are  $sp^2$  hybridized. Similar considerations hold for the oxygen atom of carbonyl groups of all kinds. The two unshared pairs of electrons on oxygen both occupy  $sp^2$  orbitals. The interorbital angle is  $120^\circ$ , as expected for trigonal hybridization.

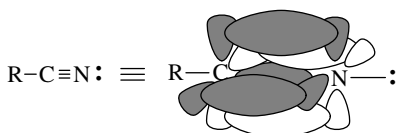


The sharing of three pairs of electrons between two atoms can be accomplished by extrapolation of the above considerations. That is, since there can only be one  $\sigma$  bond connecting the atoms, then the other two pairs of shared electrons must be in two different  $\pi$  bonds, each of which is formed by the parallel overlap of a p orbital. Furthermore the  $\pi$  bonds must be mutually orthogonal so as not to violate the Pauli exclusion principle. Hybridization of one s orbital and one p orbital gives two equivalent sp hybrid AOs which are linearly opposite to one another.

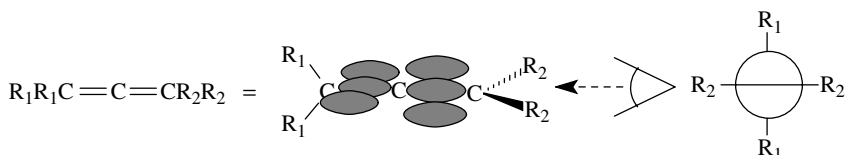


The two remaining p atomic orbitals, which are mutually orthogonal, are used to produce two orthogonal  $\pi$  bonds. The geometry of triply bonded systems is thus linear about the triple bond.

Similar considerations apply to the triply bonded nitrogen found in nitriles. The sp-hybridized carbon and nitrogen atoms form an sp-sp  $\sigma$  bond and two 2p-2p  $\pi$  bonds between carbon and nitrogen. The unshared pair on nitrogen occupies an sp hybrid orbital.



Another instance where sp hybridization is required occurs in molecules with cumulated double bonds such as allenes, ketenes, and carbodiimides. The end atoms of the cumulated units are sp<sup>2</sup> hybridized because each shares two electron pairs with another element (the central carbon) and there is a  $\sigma$  and a  $\pi$  bond. The structure, however, requires that two  $\pi$  bonds originate from the central carbon—one  $\pi$  bond going toward one end of the cumulated system, the other  $\pi$  bond going toward the other end. Thus two 2p AOs are required for  $\pi$  bonding from the central carbon and sp hybridization is appropriate. Consequently the geometry is linear at the middle atom and trigonal at the end atoms. A further consequence of the orthogonal  $\pi$  bonds is that planar bonds originating at the end carbons lie in two orthogonal planes with a dihedral angle of 90°. (A dihedral angle is the angle made by two intersecting planes.)



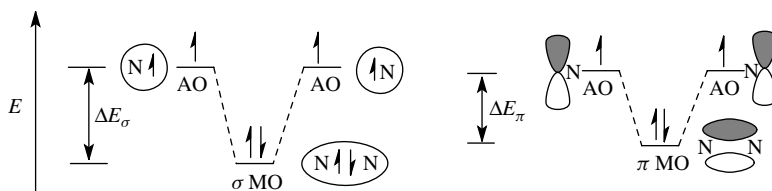
Besides providing a theoretical framework by which the structure, geometry, and octet structure of bonded elements can be explained and understood, the concept of hybridization also predicts the ordering of stabilities and energies of bonds and the energy of lone pairs of electrons in hybrid orbitals. Because s AOs are of lower energy than p AOs, hybrid orbitals with a greater proportion of s character should be more stable and thus form stronger bonds. Unshared pairs of electrons in hybrid orbitals with greater s character should also be of lower energy (more stable). As the percentage of s character of hybrid orbitals increases in the order  $sp^3$ –25% s character <  $sp^2$ –33% s character <  $sp$ –50% s character, it is found that the strength of bonds formed by overlap with those orbitals increases in a parallel fashion. For example, the bond dissociation energies of primary C–H bonds have been measured and fall in the order that is predicted by the percentage of s character of the hybrid orbitals on carbon:  $sp^3$  C–H, 105 kcal/mol;  $sp^2$  C–H, 111 kcal/mol; and  $sp$  C–H, 133 kcal/mol. Electron pairs are more stable in orbitals with more s character; thus the acidities of primary C–H bonds are found to be  $sp^3$  C–H,  $pK_a = 50$ ;  $sp^2$  C–H,  $pK_a = 44$ ; and  $sp$  C–H,  $pK_a = 25$ . This is due to the fact that the anions formed by proton removal give carbanions that have the negative charge in  $sp^3$ ,  $sp^2$ , and  $sp$  orbitals, respectively. Because the lone pair is more stable in an orbital of greater s character, the anion formed by removal of an  $sp$  C–H proton is more stable (and hence the proton is more easily removed) than the anion formed by removal of an  $sp^2$  C–H proton, which in turn is more stable (and hence the proton is more easily removed) than the anion formed by removal of an  $sp^3$  C–H proton. Other examples of the effects of greater s character in orbitals are encountered routinely.

The concept of hybridization of AOs to give new hybrid AOs involved in the bonding patterns of atoms is a useful and practical way to describe the way in which functional groups are constructed. It provides a rationale for the structure as well as the geometry and electron distribution in functional groups and molecules in which they are found. It can also be used to predict reactivity patterns of functional groups based on these considerations.

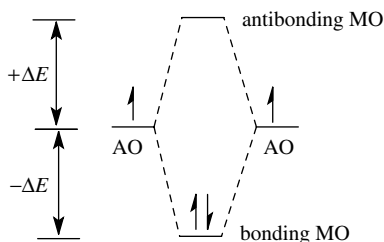
## ANTIBONDING ORBITALS

The overlap of AOs to give a new MO in which an electron pair is shared by the interacting atoms was illustrated in Figure 1.2. The new MO, which contains the shared electron pair, is of lower energy than the AOs from which it was produced by overlap. This energy change ( $\Delta E$ ) is illustrated in Figure 1.3 (N represents the *nucleus* of some element in the bond formation process). The  $\Delta E$  is related closely to the bond energy of the bond produced. The same model holds irrespective of the type of AOs which overlap (simple AOs or hybrid AOs) or the type of bond formed ( $\sigma$  or  $\pi$ ).

While this model is easy to visualize and understand, it is actually only half of the story. When AOs interact, the number of new MOs which are produced



**Figure 1.3** Energy changes that occur during the overlap of AOs to form covalent bonds.

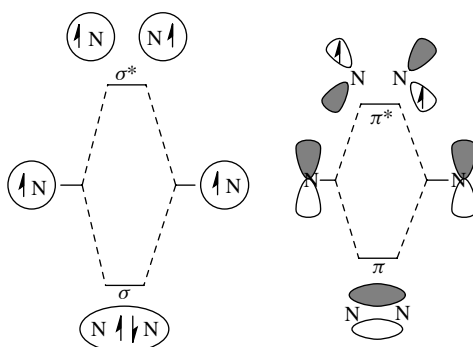


**Figure 1.4** Formation of bonding and antibonding MOs from the overlap of AOs.

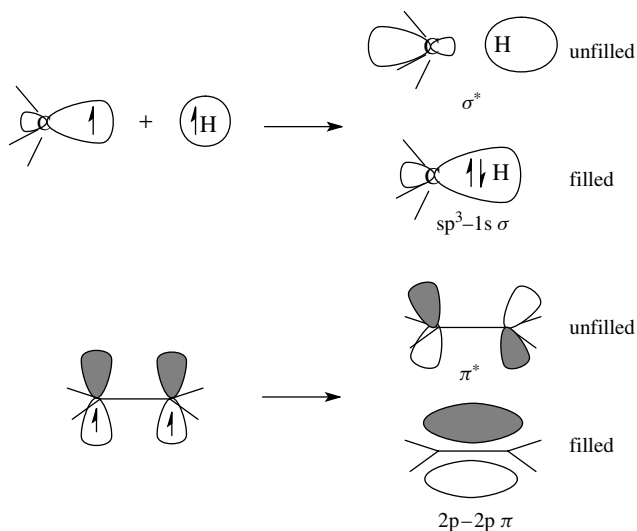
from that interaction must equal the number of AOs which initially interact. Furthermore, for each MO produced which is lower in energy than the energy of the interacting AOs, there will be one produced which will be *higher* in energy by the same amount (Figure 1.4). So when two half-filled AOs interact, there will be two MOs produced, one of lower energy which will contain the electron pair and is termed the *bonding* MO. The second molecular orbital is of higher energy, is unfilled, and is termed the *antibonding* MO.

For each bond in a molecule which is described by the overlap of AOs, there will be a bonding MO which is of lower energy and when filled with an electron pair gives rise to a stable bond between elements. There will also be an antibonding MO which is of higher energy and thus unfilled. Antibonding orbitals correspond to the situation where nuclei are moved to within the bonding distance of one another but there is *no* electron sharing; in fact the electrons and nuclei actually repel one another. This electronic and nuclear repulsion is what increases the energy of the antibonding level. Because the bonding MO is filled and the antibonding MO is unfilled, the system is at a lower net energy than the individual AOs and bond formation takes place. This occurs for both  $\sigma$  and  $\pi$  bonds as shown in Figure 1.5 (the antibonding orbitals are indicated by the asterisk). Overlap of an  $sp^3$  AO on a carbon with a  $1s$  AO on a hydrogen gives a  $\sigma$ -bonding MO that is filled with two electrons and an unfilled, higher energy, antibonding MO termed a  $\sigma^*$  MO. Likewise, overlap of two  $2p$  AOs on carbon gives a  $\pi$  MO which contains a shared pair of  $e^-$  and a  $\pi^*$  MO which is of higher energy and is unfilled.





**Figure 1.5** Formation of  $\sigma$  and  $\pi$  bonding orbitals and  $\sigma^*$  and  $\pi^*$  antibonding orbitals in a double bond between two atoms (N).

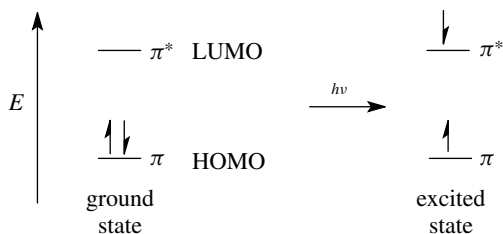


Thus far it would appear that antibonding orbitals are real orbitals, but they seem to be merely mathematical artifacts since they are unfilled and thus do not enter into bonding or energy considerations. For ground-state molecules this is actually true—all of the electrons are found in bonding orbitals. Why, then, should we even concern ourselves with their existence?

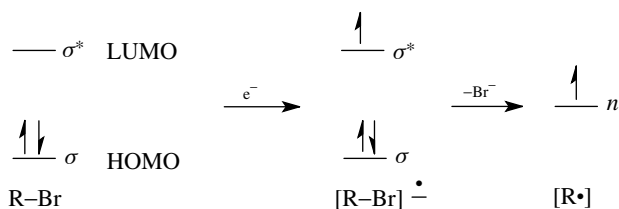
The answer lies in the realization that antibonding orbitals are still, in fact, orbitals. They are regions of space where one could have electrons. In ground-state molecules, electrons fill the lower energy bonding orbitals. Suppose, however, you wished to take an electron out of a bonding orbital and move it to a higher level. Where would it go? Or suppose you wished to add electrons to a molecule which already had its bonding orbitals filled. Where would the

electrons go? Suppose an electron-rich reagent were to donate electrons to a molecule. Where would the electrons go?

In these examples the electrons could go into a higher energy, unfilled MO which could be a nonbonding orbital (when one is present) or an antibonding orbital (which is always present). Thus it is most common to have the electrons go into an antibonding MO. Although they are of high energy, antibonding orbitals are usually unfilled and can accept electrons from several sources if sufficient energy is available to promote electrons into the antibonding energy level. Absorption of light energy can cause an electron to be promoted from the highest occupied molecular orbital (HOMO), which is usually a bonding MO, to the lowest unoccupied molecular orbital (LUMO), which is most often an antibonding MO. For example, if an olefin which contains a carbon-carbon  $\pi$  bond is exposed to ultraviolet light of the correct frequency (and hence energy), the molecule can absorb the energy of the light by promoting a  $\pi$  electron from the bonding MO into the antibonding MO. This new electronic state is termed an excited state and is higher in energy than the initial electron-paired state called the ground state. (The electron spins can be paired in the singlet excited state or unpaired in the triplet excited state.) Excited states of molecules are high-energy states which are much more reactive than ground states and can be described in terms of the population of antibonding orbitals. Consequently, almost all photochemical reactions which occur by the reactions of excited-state species are intimately dependent on the existence of and population of antibonding orbitals.

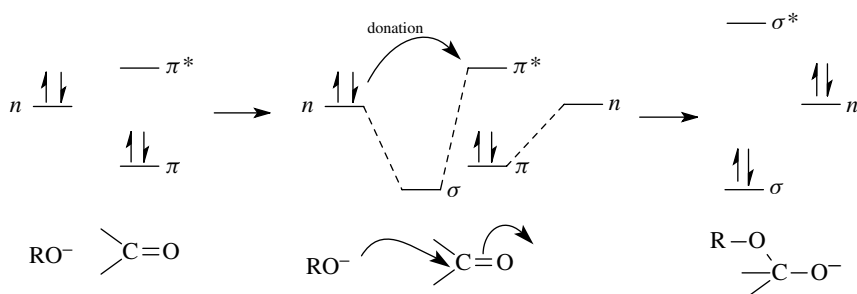


The reduction of organic molecules by the addition of electrons can take place by chemical reagents or at the surface of electrodes. In either case electrons are added to the organic compound, thus reducing it. Now electrons cannot just go anywhere; they must go into an unfilled orbital. Thus, during a reduction, electrons are injected into the LUMO of the molecule, which is often an antibonding orbital. Population of the antibonding orbital raises the total energy of the molecule and subsequent reactions follow. The electrochemical reduction of alkyl bromides illustrates the process well. An electron is added into the  $\sigma^*$  orbital of the carbon-bromine bond, which is the LUMO of a saturated alkyl bromide. Population of the antibonding orbital raises the energy of the molecule and weakens the carbon-bromine bond, which then dissociates to give bromide ion and a carbon-centered free radical which has an unpaired electron in a hybrid AO (nonbonded energy level).



Almost all dissolving metal and electrochemical reductions follow this same general sequence. An electron is donated into an unfilled orbital which is usually an antibonding MO, the energy of the molecule is raised, and chemical change ensues.

When a nucleophile attacks an electrophile, it donates a pair of electrons to the electrophile. Electron donation must take place by an overlap interaction between a filled orbital on the nucleophile which contains the electron pair to be donated and an unfilled orbital (LUMO) on the electrophile, which is usually an antibonding orbital. Population of the LUMO by electron donation raises the energy of the system leading to bonding change and new bond formation. Addition of an alkoxide to a ketone is a typical example of the process. The electron pair to be donated is in a hybrid AO and therefore is at a nonbonding energy level ( $n$ ). Overlap with the  $\pi^*$  orbital of the carbonyl group starts to populate the  $\pi^*$  orbital. This weakens the  $\pi$  bond, and the carbon-oxygen  $\pi$  bond of the carbonyl group is broken and a new lower energy  $\sigma$  bond is formed between the oxygen of the alkoxide and the carbonyl carbon. The electrons of the  $\pi$  bond end up in a nonbonding AO on oxygen in the product. This process is shown schematically.

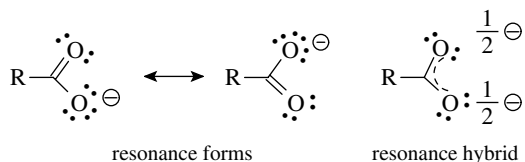


Nucleophilic additions and substitutions are the most widespread of all organic reactions, and all have the same general orbital requirements. An orbital containing an electron pair of the nucleophile overlaps with an antibonding orbital of the electrophile, which leads to population of the antibonding level (in most cases). This raises the energy of the system and bond and electron reorganization follows to give products. The electron pair must be able to be donated (i.e., not tightly bound or of higher energy) and the antibonding orbital be of sufficiently low energy to ensure effective overlap.

Thus it is seen that, although antibonding orbitals are not a major factor in describing the bonding of ground-state molecules, they can play a pivotal role in the reactions of molecules. Therefore it is important to keep in mind the existence of antibonding orbitals and their ability to accept electrons and control the reactivity of molecules.

## RESONANCE

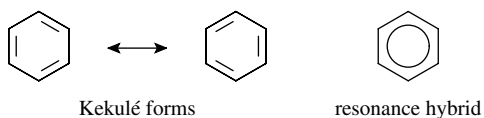
Valence shell electrons of the atoms in a molecule are either shared or unshared. The shared electrons are found in either  $\sigma$  or  $\pi$  bonds. Unshared electrons are found in AOs (usually hybrid AOs for first-row elements). Lewis structures provide a way to indicate the shared and unshared pairs of electrons in molecules. Sometimes, however, it is possible to indicate the electron distribution in molecules by more than one Lewis structure. For example, a carboxylate anion can be represented by two equivalent but different Lewis structures.



These structures are equivalent because they have the same numbers of bonds, unshared pairs of electrons, and the same charge. They are different because the negative charge is located on different oxygen atoms. Moreover the bonds from carbon to a particular oxygen are double in one structure and single in the other. When more than one correct Lewis structure can be written for a molecule, each structure is a resonance form of the molecule. The actual molecule is a resonance hybrid of the contributing resonance forms, and its properties result from a combination of the properties of the contributing resonance forms. Thus each oxygen atom carries a  $-\frac{1}{2}$  charge, and the bonds between carbon and each oxygen atom have a bond order of 1.5 and are of the same length.

A very good analogy is a mule. A mule is a hybrid of a horse and a donkey. A mule is neither a horse nor a donkey but it has properties of each. The resonance hybrid of the carboxylate anion is a resonance hybrid of the contributing resonance forms and has properties of each.

Another classic example of resonance is the benzene molecule. The localized resonance forms are termed Kekulé forms (after Friedrich August Kekulé, who first deduced the structure of benzene) and have alternating single and double bonds between carbon atoms. The actual benzene molecule is a resonance hybrid of the contributing resonance forms as the bond lengths are equal (single and double bonds have different lengths).

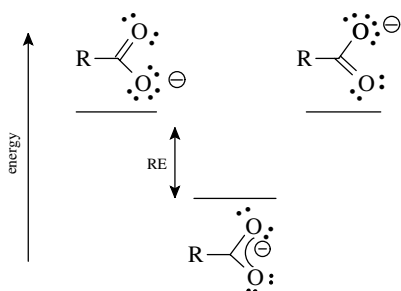


The bond order is between one (single) and two (double). The resonance hybrid is often pictured with a circle in the ring to indicate the delocalized electron distribution in the molecule.

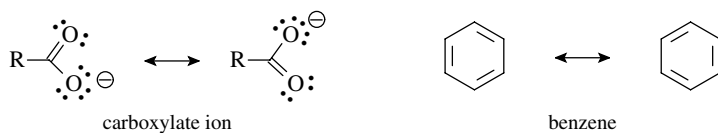
Double-headed arrows are used to indicate resonance forms. It is important to note that resonance forms are not in equilibrium, just as a mule is not a horse part of the time and a donkey the rest of the time.

The presence of resonance forms means that the electrons are not localized between two nuclei but are delocalized over more than two nuclei. The result of electron delocalization is that electrons are attracted by a greater number of nuclei, which leads to a lower energy for the molecule and hence greater stability. Simply put, resonance delocalization is a stabilizing feature of molecules.

A molecule for which resonance forms can be written is more stable than any of the contributing resonance forms. Thus the carboxylate ion (a resonance hybrid) is more stable than either of the contributing resonance forms. The difference in energy between the energy of the molecule and the energy of the most stable resonance form is the resonance energy (RE) of the molecule. The resonance energy represents the stabilization of the molecule due to the delocalization of electrons.

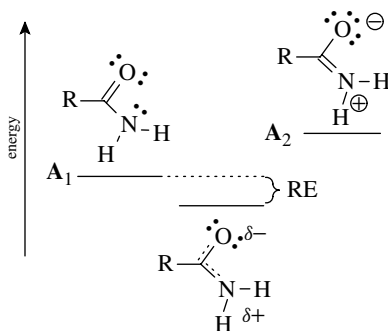


The amount of resonance energy is related to the relative energies of the contributing resonance forms. The greatest resonance stabilization is found when the contributing resonance forms are degenerate (equal) in energy. Thus molecules such as the carboxylate ion, benzene, the allyl anion, and the allyl cation all have significant resonance stabilization because the main resonance contributors are of the same energy.

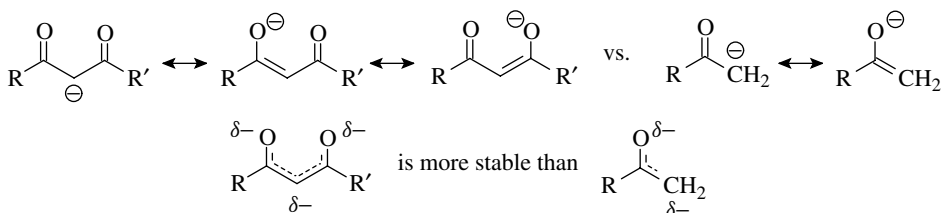




In contrast, resonance stabilization is less in an amide because the resonance forms  $A_1$  and  $A_2$  given below are very different in energy. Nevertheless, because an amide is a resonance hybrid of  $A_1$  and  $A_2$ , it is predicted that there should be some double-bond character in the bond between carbon and nitrogen. This is in fact the case since many amides show restricted rotation around the C–N bond (typical of a  $\pi$  bond). Moreover, the nitrogen atom in amides is nearly planar and not very basic, also indicating that the lone pair is delocalized.



It is also generally true that the greater the number of contributing resonance forms, the greater will be the resonance stabilization. For this reason the enolate of a  $\beta$ -diketone has much more resonance stabilization than the enolate of a simple ketone (three resonance forms versus two). The electrons are delocalized over five atoms in the former versus three atoms in the latter. In addition, the electron density on the carbon atom is less in the diketone enolate than in a simple methyl ketone enolate.

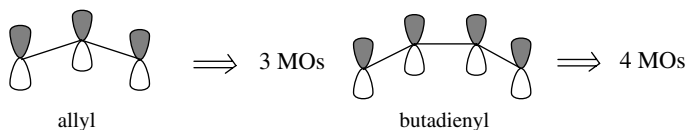


Resonance has a significant influence on the electron distributions and energies of molecules. The delocalization of electrons is described by the contributions of resonance forms, which are themselves localized structures with discrete bonds. Such structures are known as valence bond (VB) structures, and this approach

to the description of bonding in molecules is called the valence bond approach. As long as one keeps in mind that resonance forms are limiting VB structures and that the actual molecule is a resonance hybrid of these VB structures, a great deal of insight into the structure and properties of molecules can be gained.

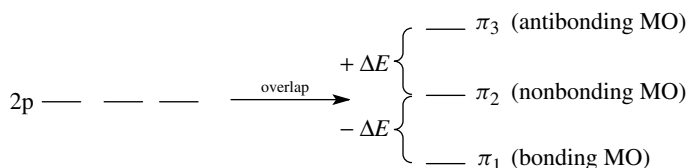
## CONJUGATED $\pi$ SYSTEMS

Another way to describe delocalized bonding uses the MO approach. The same principles of overlap of AOs can be applied to systems where more than two p AOs overlap to form  $\pi$  systems. First, the number of MOs produced by the overlap will be the same as the number of atomic p orbitals which interact. Thus for the allyl system where three contiguous p orbitals interact, there will be three MOs produced from the interaction of three 2p AOs. For the butadienyl system where there are four contiguous p orbitals interacting, four MOs will result, and so on.



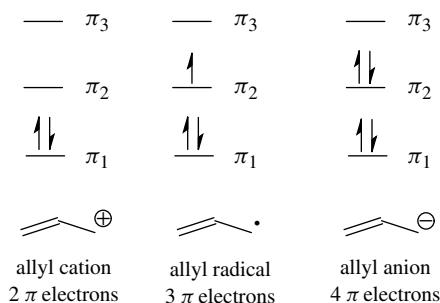
Second, the energy distribution of the MOs will be disposed symmetrically about the energy of the AOs before they interact (nonbonded energy level). This means that the total energy of the bonding MOs is offset by the total energy of the antibonding MOs. For example, if one MO is of lower energy by  $-\Delta E$  due to overlap, then there must be an antibonding MO raised to higher energy ( $+\Delta E$ ). Molecular orbitals which are lower in energy than the nonbonding energy are bonding MOs ( $-\Delta E$ ), those which are higher in energy than the nonbonding energy are antibonding MOs ( $+\Delta E$ ), and those at the same energy as the nonbonding energy are nonbonding MOs ( $\Delta E = 0$ ).

For the allyl system which has 3 MOs from the overlap of three 2p AOs, one MO will be lowered in energy ( $-\Delta E$ ) and so one MO will be raised by the same amount. The remaining MO must stay at the nonbonding level ( $\Delta E = 0$ ) to maintain energy symmetry around the nonbonding level.

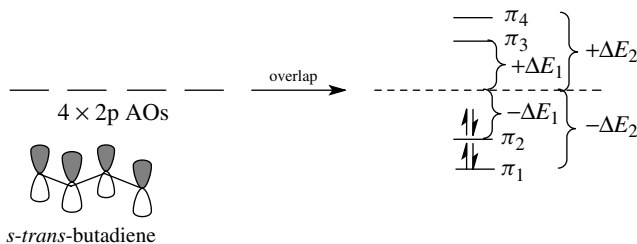


What is interesting is that this overlap model allows the orbital diagram to be constructed without concerning itself with electrons. The MOs produced by the

interaction of AOs can each hold two paired electrons, and these can be filled in depending on the number of electrons present in the  $\pi$  system. Thus the bonding diagrams for the allyl cation, allyl radical, and allyl anion can be constructed by merely filling the orbitals with the number of  $\pi$  electrons present in these species (two, three, and four  $\pi$  electrons, respectively). This orbital picture also demonstrates that all three intermediates in the allyl system are stabilized because each contains two electrons in the  $\pi_1$ -bonding MO and any remaining electrons are in the nonbonding orbital.



Two of the four MOs of the butadienyl system are at lower energy than the nonbonded energy level ( $-\Delta E_1, -\Delta E_2$ ), and two are at higher energy than the nonbonded energy level ( $+\Delta E_1, +\Delta E_2$ ). The four  $\pi$  electrons of butadiene fill the two bonding MOs and give a stable molecule. It should also be obvious that butadienyl species with less than or more than four  $\pi$  electrons should be significantly less stable than butadiene itself. Removal of an electron requires energy because the electron would have to come from a relatively stable bonding MO. Addition of an electron to the butadienyl  $\pi$  system requires that it be put into an antibonding MO which is also energetically unfavorable.



A great many  $\pi$  systems have been examined by this approach and the orbital diagrams understood. As seen before, the antibonding orbitals are often unfilled in the ground state but play an important part in the excited states and reactions of these compounds.