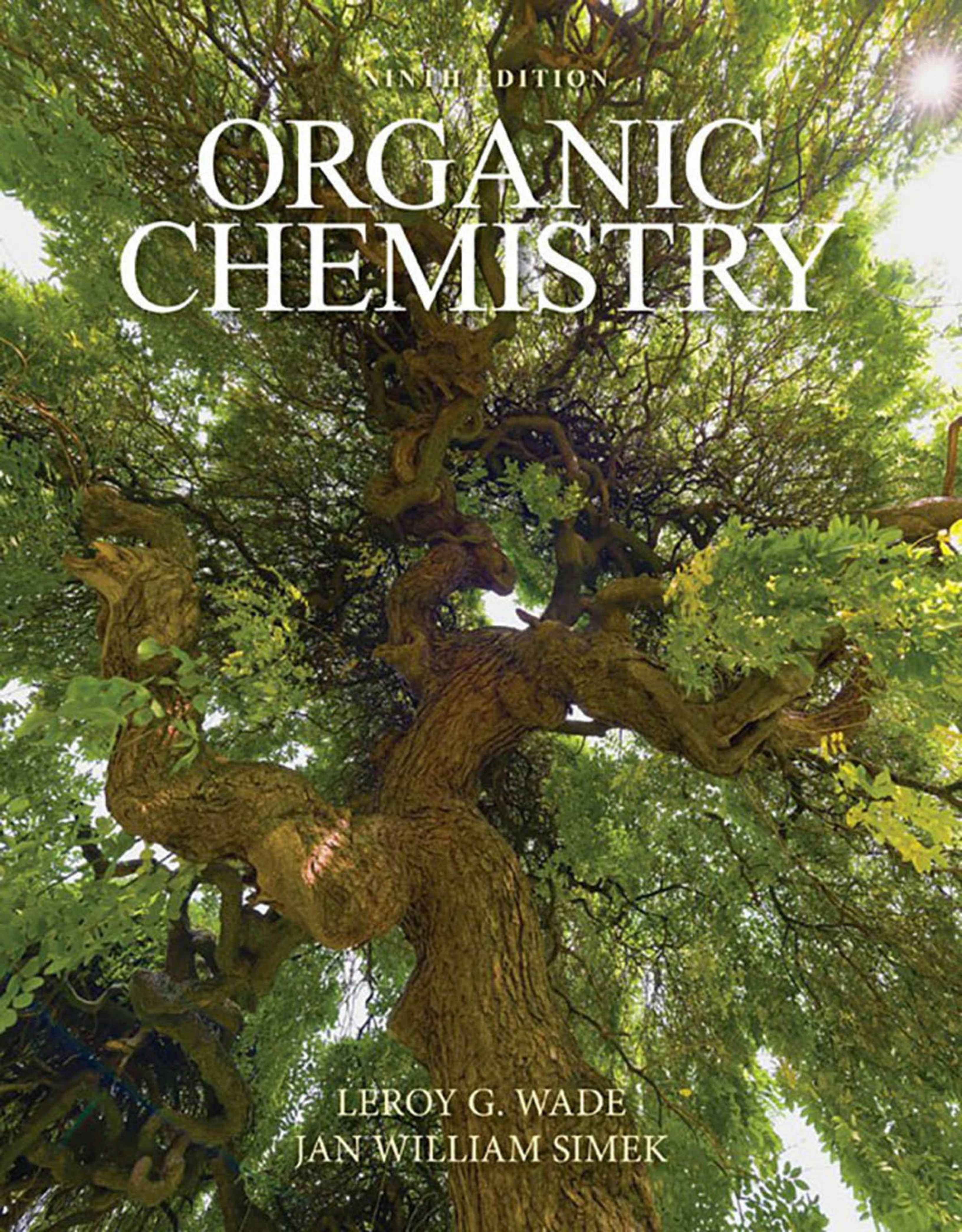

NINTH EDITION

ORGANIC CHEMISTRY

LEROY G. WADE
JAN WILLIAM SIMEK

ORGANIC CHEMISTRY

NINTH EDITION

LEROY G. WADE, JR.
WHITMAN COLLEGE

CONTRIBUTING AUTHOR:

JAN WILLIAM SIMEK
CALIFORNIA POLYTECHNIC STATE UNIVERSITY

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To my students and colleagues at Whitman College

About the Authors

L. G. "Skip" Wade decided to become a chemistry major during his sophomore year at Rice University, while taking organic chemistry from Professor Ronald M. Magid. After receiving his B.A. from Rice in 1969, Wade went on to Harvard University, where he did research with Professor James D. White. While at Harvard, he served as the Head Teaching Fellow for the organic laboratories and was strongly influenced by the teaching methods of two master educators, Professors Leonard K. Nash and Frank H. Westheimer.

After completing his Ph.D. at Harvard in 1974, Dr. Wade joined the chemistry faculty at Colorado State University. Over the course of fifteen years at Colorado State, Dr. Wade taught organic chemistry to thousands of students working toward careers in all areas of biology, chemistry, human medicine, veterinary medicine, and environmental studies. He also authored research papers in organic synthesis and in chemical education, as well as eleven books reviewing current research in organic synthesis. In 1989, Dr. Wade joined the chemistry faculty at Whitman College, where he continued to teach organic chemistry and pursue research interests in organic synthesis and forensic chemistry. Dr. Wade received the A. E. Lange Award for Distinguished Science Teaching at Whitman in 1993.

Dr. Wade's interest in forensic science has led him to testify as an expert witness in court cases involving drugs and firearms, and he has worked as a police firearms instructor, drug consultant, and boating safety officer. He also enjoys repairing and restoring old violins and bows, which he has done professionally for many years.

Jan Simek was born to humble, coal-mining parents who taught him to appreciate the importance of carbon at a very early age. At age 14, he was inspired to pursue a career teaching chemistry by his high school chemistry teacher, Joe Plaskas. Under the guidance of Professor Kurt Kaufman at Kalamazoo College, Dr. Simek began lab work in synthesis of natural products that turned into research in hop extracts for the Kalamazoo Spice Extraction Company. After receiving a master's degree from Stanford University, Dr. Simek worked in the pharmaceutical industry, synthesizing compounds designed to control diabetes and atherosclerosis, and assisted in the isolation of anti-cancer antibiotics from natural sources. Returning to Stanford University, Dr. Simek completed his Ph.D. with the legendary Professor Carl Djerassi, who developed the first synthesis of steroidal oral contraceptives.

Dr. Simek's 35-year teaching career was spent primarily at California Polytechnic State University, San Luis Obispo, where he received the university's Distinguished Teaching Award. Other teaching experiences include Albion College, the University of Colorado at Boulder, Kalamazoo College, and the University of California at Berkeley. In addition to his pharmaceutical research, he has industrial experience investigating dyes, surfactants, and liquid crystals, and he continues to consult for the biotechnology industry.

Although his outside interests include free climbing in Yosemite, performing in a reggae band, and parasailing over the Pacific, as close as he gets to any of those is tending his backyard garden with his wife Judy.

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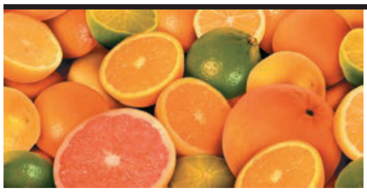

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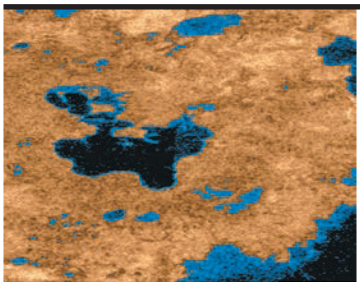

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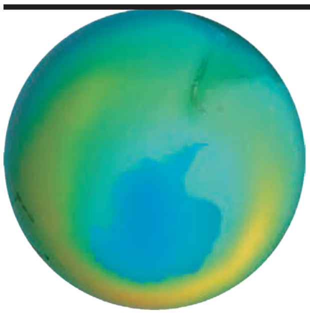

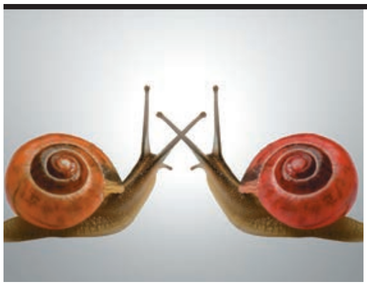

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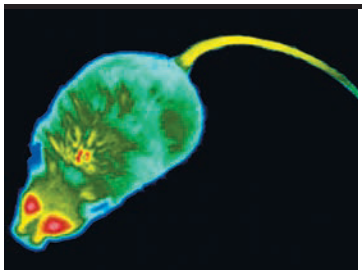

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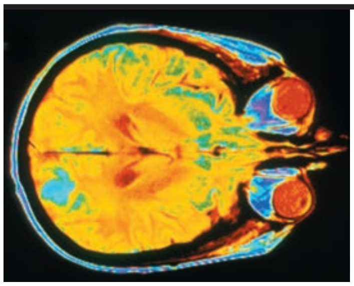

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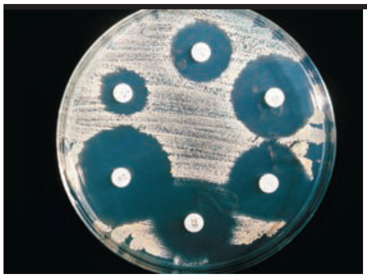

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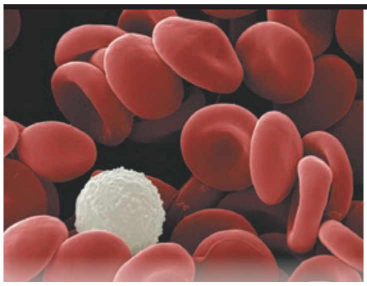

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MECHANISMS

MECHANISMS (continued)

MECHANISMS (continued)

New to This Edition

1 **NEW!** Expanded coverage of **Acid/Base Chemistry** in chapter 2 and separation of the chapter on **Substitution and Elimination** into two distinct chapters allow students to build upon their existing knowledge and move through their first mechanisms with greater clarity and with more opportunities to test and apply their understanding without getting overwhelmed by organic chemistry. New problem-solving strategy spreads have been added to both corresponding chapters for additional support.

2 **NEW! Reaction Starbursts/Reaction Maps** appear before the end of every 'reaction-based' chapter to help students better understand and mentally organize reactive similarities and distinctions.

3 **NEW! Visual Guides to Organic Reactions** place the reactions covered in each chapter within the overall context of the reactions covered in the course.

4 **NEW! Problem Solving Strategies** have been added and explicitly highlighted in several chapters, including new strategies for resonance, acid-base equilibria, and multistep synthesis.

5 **NEW! Over 100 New Problems** include more synthesis problems and problems based on recent literature.

6 **NEW! Green Chemistry** is emphasized with presentation of less toxic, environmentally friendly reagents in many situations, such as oxidation of alcohols with bleach rather than with chromium reagents.

7 **NEW! Chapter Openers** focus on organic applications, with introductions and images for a more enticing, contemporary presentation.

8 **20 Key Mechanism Boxes** highlight the fundamental mechanistic principles that recur throughout the course and are the basis for some of the longer, more complex mechanisms. Each describes the steps of the reaction in detail with a specific example to reinforce the mechanism and a concluding problem to help students absorb these essential reactions.

9 **NEW! Explanations and Annotations to Mechanisms** help students better understand how each mechanism works.

Brief Chapter-by-Chapter Changes

Global Changes

Every chapter begins with a new chapter-opening photograph showing an interesting, real-world application of the material in that chapter. New Problem-Solving Hints and new Applications have been added to each chapter, and all of the chapters have gone through a careful revision process. All of the structures have been updated to the new IUPAC recommendations for showing stereochemistry. Green curved arrows are used to show the imaginary flow of electrons in resonance forms, in contrast to the red curved arrows used to show the actual flow in reactions.

Chapter 1 Structure and Bonding

- The material on structure, bonding, and molecular geometry has been consolidated into one chapter. A revised discussion of resonance includes a Problem-Solving Strategy, a Problem-Solving Hint on the types of arrows used in organic chemistry, and several new problems.

Chapter 2 Acids and Bases; Functional Groups

- The presentation of acids and bases has been moved from the previous Chapter 1 and greatly enhanced to become the main subject in the new Chapter 2. The new material includes sections on inductive, hybridization, resonance, and solvent effects on acidity and basicity; a section and Problem-Solving Strategy on predicting acid-base equilibrium positions; new Problem-Solving Hints; new figures; new applications; and 18 new problems.

Chapter 4 The Study of Chemical Reactions

- The values of bond dissociation enthalpies have been updated to the most recent experimental results throughout the chapter. A revised discussion of Hammond's postulate includes a figure that has been revised for clarity.

Chapter 5 Stereochemistry

- This chapter includes a revised summary of types of isomers, with revised figures for clarity. There are new Problem-Solving Hints on stereocenters, Fischer projections, and relative versus absolute configurations.

Chapter 6 Alkyl Halides; Nucleophilic Substitution

- The sections on E1 and E2 eliminations have been moved to Chapter 7. A new graphic showing the strengths of common nucleophiles has been added, and the summary of nucleophilic substitution conditions has been expanded. Several Problem-Solving Hints have been added on nucleophiles and bases, acid-base strength in the S_N1 reaction, and carbocation rearrangements.

Chapter 7 Structure and Synthesis of Alkenes; Elimination

- This chapter now contains expanded sections on E1 and E2 eliminations. Several Problem-Solving Hints have been added, as well as graphics on the competition between substitutions and eliminations. Several new problems have been added, including two solved problems.

Chapter 8 Reactions of Alkenes

- Several diagrams, applications, problems, and starburst summaries of reactions have been added. The new visual *Guide to Organic Reactions* is introduced in Chapter 8, and further updated in Chapters 11, 17, 18, 21, and 22.

Chapter 9 Alkynes

- New examples and a new starburst summary have been added. A new Problem-Solving Hint summarizes oxidative cleavages of alkynes.

Chapter 10 Structure and Synthesis of Alcohols

- The material on lithium dialkylcuprates has been expanded into a new section. New Problem-Solving Hints on Grignard reactions and organometallic reactions have also been added. A new starburst reaction summary has been added.

Chapter 11 Reactions of Alcohols

- A newly revised discussion of oxidizing agents emphasizes "green" reactions with sodium hypochlorite and acetic acid, or TEMPO, rather than toxic chromium reagents. A new interim summary compares alcohol oxidations with and without chromium reagents, and a new Problem-Solving Hint discusses ring-size changes and rearrangements. Two new starburst reaction summaries have been added.

Chapter 14 Ethers, Epoxides, and Thioethers

- New material and a new graphic have been added to clarify the regiochemistry of the opening of substituted epoxides. Several new problems have been added.

Chapter 15 Conjugated Systems, Orbital Symmetry, and Ultraviolet Spectroscopy

- Several figures have been revised for clarity, and new applications have been added.

Chapter 16 Aromatic Compounds

- New to this chapter are a Problem-Solving Hint on drawing energy diagrams for the MOs of cyclic systems, plus new applications and problems. A new starburst reaction summary has also been added.

Chapter 17 Reactions of Aromatic Compounds

- A new Problem-Solving Strategy has been added to explain multistep synthesis using electrophilic aromatic substitutions. The discussion of the Suzuki reaction has been expanded, including its mechanism. New applications, two new starburst reaction summaries, and several problems have also been added.

Chapter 18 Ketones and Aldehydes

- The discussion of syntheses of ketones and aldehydes has been revised to emphasize oxidations that use less toxic reagents such as bleach and TEMPO. Several new applications have been added, as well as a starburst reaction summary and several new problems.

Chapter 19 Amines

- A Problem-Solving Hint on pK_a of amines has been added, plus new applications and several new problems.

Chapter 20 Carboxylic Acids

- New problems and applications have been added as well as a starburst reaction summary.

Chapter 21 Carboxylic Acid Derivatives

- Several new problems and applications have been added, as well as a starburst reaction summary.

Chapter 22 Condensations and Alpha Substitutions of Carbonyl Compounds

- A new Problem-Solving Hint on ketone and ester carbonyl groups has been added, plus a new starburst reaction summary. Several applications and problems have been added as well.

Chapter 23 Carbohydrates and Nucleic Acids

- This chapter has been updated with a new application on glycoproteins. Some of the obsolete older reactions have been dropped.

Chapter 24 Amino Acids, Peptides, and Proteins

- The material on solid-phase peptide synthesis has been updated to use current techniques, and some of the obsolete, older methods have been deleted.

Chapter 26 Synthetic Polymers

- The organization of the chapter has been revised to emphasize chain-growth versus step-growth polymers, rather than addition versus condensation polymers. A new section has been added on the recycling of plastics, plus applications on 3D printing and PEX pipes.

Preface

To the Student

As you begin your study of organic chemistry, you might feel overwhelmed by the number of compounds, names, reactions, and mechanisms that confront you. You might even wonder whether you can learn all this material in a single year. The most important function of a textbook is to organize the material to show that most of organic chemistry consists of a few basic principles and many extensions and applications of these principles. Relatively little memorization is required if you grasp the major concepts and develop flexibility in applying those concepts. Frankly, I have a poor memory, and I hate memorizing lists of information. I don't remember the specifics of most of the reactions and mechanisms in this book, but I can work them out by remembering a few basic principles, such as "alcohol dehydrations usually go by E1 mechanisms."

Still, you'll have to learn some facts and fundamental principles to serve as the working "vocabulary" of each chapter. As a student, I learned this the hard way when I made a D on my second organic chemistry exam. I thought organic would be like general chemistry, where I could memorize a couple of equations and fake my way through the exams. For example, in the ideal gas chapter, I would memorize $PV = nRT$, and I was good to go. When I tried the same approach in organic, I got a D. We learn by making mistakes, and I learned a lot in organic chemistry.

In writing this book, I've tried to point out a small number of important facts and principles that should be learned to prepare for solving problems. For example, of the hundreds of reaction mechanisms shown in this book, about 20 are the fundamental mechanistic steps that combine into the longer, more complicated mechanisms. I've highlighted these fundamental mechanisms in *Key Mechanism* boxes to alert you to their importance. Similarly, the *Guide to Organic Reactions* appears in six chapters that contain large numbers of new reactions. This guide outlines the kinds of reactions we cover and shows how the reactions just covered fit into the overall organization. Spectroscopy is another area in which a student might feel pressured to memorize hundreds of facts, such as NMR chemical shifts and infrared vibration frequencies. I couldn't do that, so I've always gotten by with knowing about a dozen NMR chemical shifts and about a dozen IR vibration frequencies, and knowing how they are affected by other influences. I've listed those important infrared frequencies in Table 12-2 and the important NMR chemical shifts in Table 13-3.

Don't try to memorize your way through this course. It doesn't work; you have to know what's going on so you can apply the material. Also, don't think (like I did) that you can get by without memorizing *anything*. Read the chapter, listen carefully to the lectures, and *work the problems*. The problems will tell you whether or not you know the material. If you can do the problems, you should do well on the exams. If you can't do the problems, you probably won't be able to do the exams, either. If you keep having to look up an item to do the problems, that item is a good one to learn.

Here are some hints I give my students at the beginning of the course:

1. Read the material in the book before the lecture (expect 13–15 pages per lecture). Knowing what to expect and what is in the book, you can take fewer notes and spend more time listening and understanding the lecture.

2. After the lecture, review your notes and the book, and do the in-chapter problems. Also, read the material for the next lecture.

3. If you are confused about something, visit your instructor during office hours immediately, before you fall behind. Bring your attempted solutions to problems with you to show the instructor where you are having trouble.

4. To study for an exam, begin by reviewing each chapter and your notes, and reviewing any reaction summaries to make sure you can recognize and use those reactions. The “starburst” summaries are most useful for developing syntheses, since you can quickly glance at them and see the most useful conversions for that functional group. Then concentrate on the end-of-chapter problems. In each chapter, the Essential Problem-Solving Skills (EPSS) outline reviews the important concepts in the chapter and shows which problems can be used to review each concept. Also use old exams, if available, for practice. Many students find that working in a study group and posing problems for each other is particularly helpful.

Remember the two “golden rules” of organic chemistry.

1. ***Don’t Get Behind!*** The course moves too fast, and it’s hard to catch up.
2. ***Work Lots of Problems.*** Everyone needs the practice, and the problems show where you need more work.

I am always interested to hear from students using this book. If you have any suggestions about how the book might be improved, or if you’ve found an error, please let me know (L. G. Wade, Whitman College, Walla Walla, WA 99362: E-mail wadelg@whitman.edu). I take students’ suggestions seriously, and hundreds of them now appear in this book. For example, Whitman student Brian Lian suggested Figure 21-9, and University of Minnesota student (and race-car driver) Jim Coleman gave me the facts on the fuels used at Indianapolis.

Good luck with your study of organic chemistry. I’m certain you will enjoy this course, especially if you let yourself relax and develop an interest in how organic compounds influence our lives. My goal in writing this book has been to make the process a little easier: to build the concepts logically on top of each other, so they flow naturally from one to the next. The hints and suggestions for problem solving have helped my students in the past, and I hope some of them will help you to learn and use the material. Even if your memory is worse than mine (highly unlikely), you should be able to do well in organic chemistry. I hope this will be a good learning experience for all of us.

To the Instructor

In writing the first edition of this text, my goal was to produce a modern, readable text that uses the most effective techniques of presentation and review. I wanted a book that presents organic chemistry at the level needed for chemistry and biochemistry majors, but one that presents and explains the material in ways that facilitate success for all the many different kinds of students who take the course. Subsequent editions have extended and refined these goals, with substantial rewriting and reorganizing and with many new features. This ninth edition adds several new features to help students organize types of reactions and mechanisms for easier learning and better understanding, as well as for reference.

New to This Edition

To help students organize functional group reactions, new **Starburst Summaries** have been added that provide visual links between synthetically related functional groups. This new feature is particularly useful when students are developing multistep syntheses, when the visual links help them to see the possible reactions moving forward from a reactant or synthetic intermediate. The new **Guides to Organic Reactions** will help students to organize mentally the many new reactions they are learning, and where those reactions fit within the overall scheme of the types of reactions we use in organic chemistry. **Chapter-opening photographs**, with captions that explain how the photograph relates to the chemistry presented in that chapter, have been added to all of the chapters. We have tried to select photos that are remarkable in some way or another and that grab the viewer’s attention.

All of the features of the earlier editions have been retained in this ninth edition. In many cases, those that were introduced in earlier editions have been expanded and refined. Many **updated applications** have been added, including those relating to medicine, green chemistry, biochemistry, and other contemporary areas of interest. **Green chemistry** is emphasized in many areas, most notably in the use of methods that avoid chromium reagents, which are known to be toxic and carcinogenic. The older, more toxic reagents are mentioned, but they are no longer given as the first choice for a reagent. Mechanisms have been provided for the newest reactions, such as the Suzuki coupling, when they are relevant to the material and studied well enough to be confident they are correct.

Key Features

Expanded Coverage of Acids and Bases: After reviewing the basics of bonding, hybridization, and molecular structure in Chapter 1, Chapter 2 is centered around acids and bases and how these concepts apply to organic compounds. The Arrhenius, Brønsted-Lowry, and Lewis definitions are introduced and explained. The uses of pK_a and pK_b are described, followed by a discussion and a Problem-Solving Strategy feature on predicting the position of an acid-base equilibrium reaction. Factors that affect acidity and basicity are explained, including solvent effects, size, electronegativity, inductive effects, hybridization effects, and resonance effects. Lewis acid-base reactions are discussed, with a careful discussion of the correct use of the curved-arrow formalism.

Separation of Substitution and Elimination Reactions: The crucial chapters on substitution and elimination have been revised, with substitutions covered in Chapter 6 and eliminations in Chapter 7. This organization allows students to become more comfortable with the differences between S_N1 and S_N2 substitutions before the possible reaction pathways are expanded to include eliminations. Chapter 7 presents complete coverage of the competition between substitutions and eliminations, and how one can predict what mechanisms and products are most likely.

Organic Synthesis: Many new synthetic problems have been added, some of them coming from the recent literature. The material on organic synthesis and retrosynthetic analysis has been supplemented, with particular attention to multistep aromatic syntheses.

Nomenclature: We have tried to stay as current as possible with the constantly changing IUPAC nomenclature, and this edition reflects some of the most recent changes. Beginning with the eighth edition, we have used the 1993 IUPAC positioning of the locants in names (e.g., but-1-ene), while also showing the names using the older positions of the locants (e.g., 1-butene). We have also carefully defined stereochemical terms (such as *stereocenter* and *chiral center*) correctly and precisely, and we have endeavored to use the most precise term in each case.

In this edition, we have adopted three of the newest changes in the IUPAC rules:

1. In showing stereochemistry, IUPAC now recommends the "reverse perspective" (closer end is smaller) version of wedged dashed bonds. Wedged solid bonds are still drawn with normal perspective, with their closer end larger.
2. IUPAC now defines *hydroxyl* as referring only to the radical, not the functional group. The functional group is the *hydroxy group*. We have changed these terms where needed to conform to this rule.
3. At one time, the IUPAC banished the term *ketal*. It has now been reinstated as a subclass of acetals, and we have resumed using it.

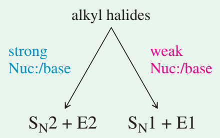
This ninth edition also includes a new Nomenclature Appendix, which serves as a compact reference to the rules of naming organic compounds. This feature should make it easier for students to name compounds without always having to find the discussion pertaining to that particular functional group.

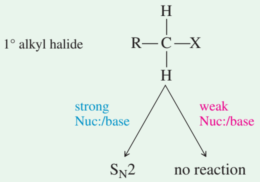
The Keys to Organic Chemistry

Wade & Simek's ninth edition of *Organic Chemistry* presents key principles of organic chemistry in the context of fundamental reasoning and problem solving. Written to reflect how today's students use textbooks, this text serves as a primary guide to organic chemistry, as well as a comprehensive study resource when working problems and preparing for exams.

The resources in this book include Problem-Solving Strategies throughout, plus Partially Solved Problems, Reaction Summaries, new Starburst Summaries, and new Reaction Guides. Through a careful, refined presentation and step-by-step guidance, this ninth edition gives students a contemporary overview of organic chemistry with tools for organizing and understanding reaction mechanisms and synthetic organic chemistry.

PROBLEM-SOLVING STRATEGY Predicting Substitutions and Eliminations





Given a set of reagents and solvents, how can you predict what products will result and which mechanisms will be involved? Should you memorize all this theory about substitutions and eliminations? Students sometimes feel overwhelmed at this point.

Memorizing is not the best way to approach this material because the answers are not absolute and too many factors are involved. Besides, the real world with its real reagents and solvents is not as clean as our equations on paper. Most nucleophiles are also basic, and many solvents can solvate ions or react as nucleophiles or bases.

The first principle you must understand is that *you cannot always predict one unique product or one unique mechanism*. Often, the best you can do is to eliminate some of the possibilities and make some accurate predictions. Remembering this limitation, here are some general guidelines:

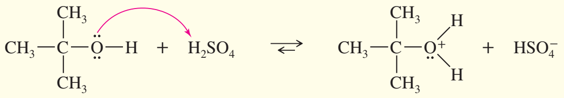
1. **The strength of the base or nucleophile determines the order of the reaction.** If a strong nucleophile (or base) is present, it will force second-order kinetics, either S_N2 or E2. If no strong base or nucleophile is present, you should consider first-order reactions, both S_N1 and E1. Addition of silver salts to the reaction can force some difficult ionizations.
2. **Primary halides usually undergo the S_N2 reaction, occasionally the E2 reaction.** Primary halides rarely undergo first-order reactions, unless the carbocation is resonance-stabilized. With good nucleophiles, S_N2 substitution is usually observed. With a strong base, E2 elimination may occasionally be observed.

SOLVED PROBLEM 7-7

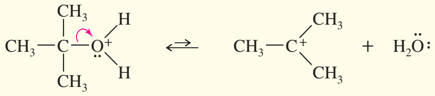
(a) Propose a mechanism for the sulfuric acid-catalyzed dehydration of *tert*-butyl alcohol.

SOLUTION

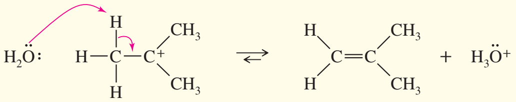
The first step is protonation of the hydroxy group, which converts it to a good leaving group.



The second step is ionization of the protonated alcohol to give a carbocation.



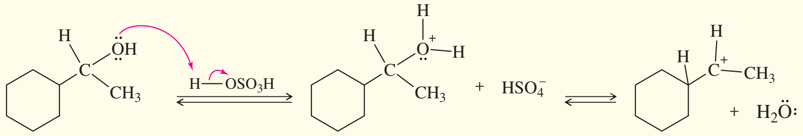
Abstraction of a proton completes the mechanism.



(b) Predict the products and propose a mechanism for the acid-catalyzed dehydration of 1-cyclohexylethanol.

PARTIAL SOLUTION:

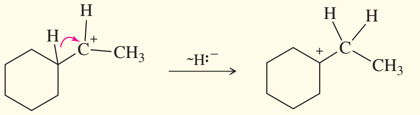
Protonation of the hydroxy group, followed by loss of water, forms a carbocation.



1-cyclohexylethanol

carbocation

The carbocation can lose a proton, or it can rearrange to a more stable carbocation.



unrearranged 2° carbocation

rearranged 3° carbocation

PROBLEM-SOLVING HINT

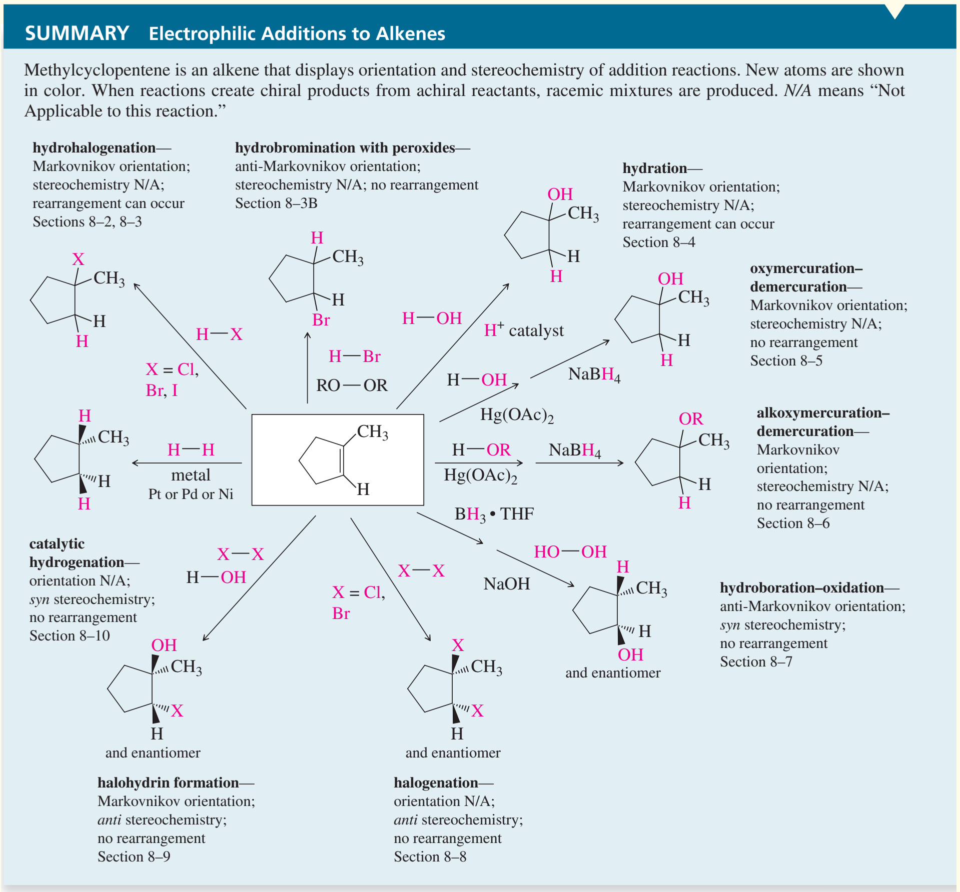
Alcohol dehydrations usually go through E1 elimination of the protonated alcohol.

Reactivity is: 3° > 2° >> 1°

Rearrangements are common.

Protonated primary alcohols dehydrate at elevated temperatures with rearrangement (E1), or the adjacent carbon may lose a proton to a weak base at the same time water leaves (E2).

Principles, Preparation, and Problem Solving



SUMMARY Electrophilic Additions to Alkenes

Methylcyclopentene is an alkene that displays orientation and stereochemistry of addition reactions. New atoms are shown in color. When reactions create chiral products from achiral reactants, racemic mixtures are produced. *N/A* means "Not Applicable to this reaction."

hydrohalogenation—Markovnikov orientation; stereochemistry N/A; rearrangement can occur Sections 8–2, 8–3

hydrobromination with peroxides—anti-Markovnikov orientation; stereochemistry N/A; no rearrangement Section 8–3B

hydration—Markovnikov orientation; stereochemistry N/A; rearrangement can occur Section 8–4

oxymercuration–demercuration—Markovnikov orientation; stereochemistry N/A; no rearrangement Section 8–5

alkoxymercuration–demercuration—Markovnikov orientation; stereochemistry N/A; no rearrangement Section 8–6

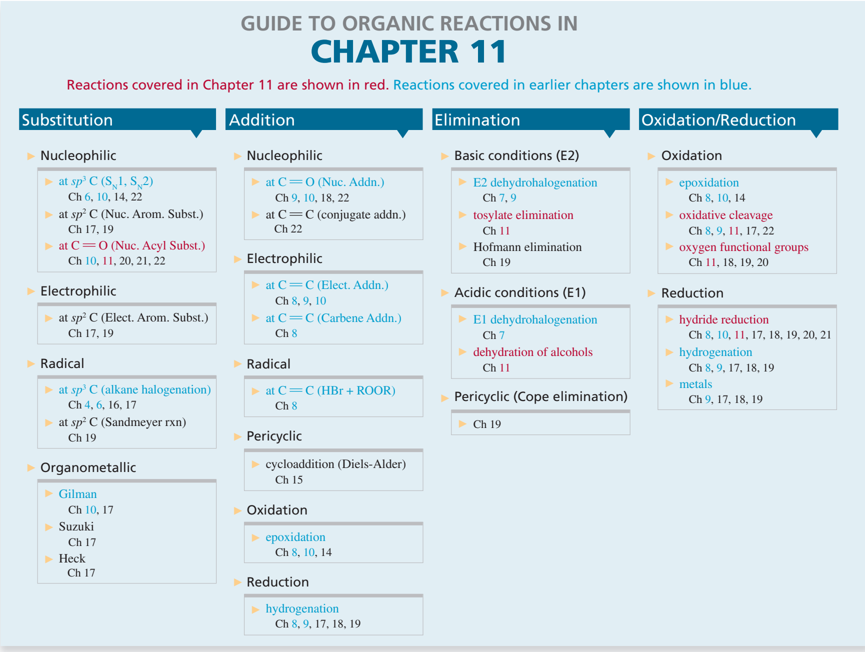
catalytic hydrogenation—orientation N/A; *syn* stereochemistry; no rearrangement Section 8–10

hydroboration–oxidation—anti-Markovnikov orientation; *syn* stereochemistry; no rearrangement Section 8–7

halohydrin formation—Markovnikov orientation; *anti* stereochemistry; no rearrangement Section 8–9

halogenation—orientation N/A; *anti* stereochemistry; no rearrangement Section 8–8

NEW! Starburst Reaction Summaries appear before the end-of-chapter material of "reaction-based" chapters to help students mentally organize the reactions and recognize their similarities and differences.



GUIDE TO ORGANIC REACTIONS IN

CHAPTER 11

Reactions covered in Chapter 11 are shown in red. Reactions covered in earlier chapters are shown in blue.

Substitution

- Nucleophilic
  - at sp^3 C (S_N1, S_N2) Ch 6, 10, 14, 22
  - at sp^2 C (Nuc. Arom. Subst.) Ch 17, 19
  - at C=O (Nuc. Acyl Subst.) Ch 10, 11, 20, 21, 22
- Electrophilic
  - at sp^2 C (Elect. Arom. Subst.) Ch 17, 19
- Radical
  - at sp^3 C (alkane halogenation) Ch 4, 6, 16, 17
  - at sp^2 C (Sandmeyer rxn) Ch 19
- Organometallic
  - Gilman Ch 10, 17
  - Suzuki Ch 17
  - Heck Ch 17

Addition

- Nucleophilic
  - at C=O (Nuc. Addn.) Ch 9, 10, 18, 22
  - at C=C (conjugate addn.) Ch 22
- Electrophilic
  - at C=C (Elect. Addn.) Ch 8, 9, 10
  - at C=C (Carbene Addn.) Ch 8
- Radical
  - at C=C (HBr + ROOR) Ch 8
- Pericyclic
  - cycloaddition (Diels-Alder) Ch 15
- Oxidation
  - epoxidation Ch 8, 10, 14
- Reduction
  - hydrogenation Ch 8, 9, 17, 18, 19

Elimination

- Basic conditions (E2)
  - E2 dehydrohalogenation Ch 7, 9
  - tosylate elimination Ch 11
  - Hofmann elimination Ch 19
- Acidic conditions (E1)
  - E1 dehydrohalogenation Ch 7
  - dehydration of alcohols Ch 11
- Pericyclic (Cope elimination)
  - Ch 19

Oxidation/Reduction

- Oxidation
  - epoxidation Ch 8, 10, 14
  - oxidative cleavage Ch 8, 9, 11, 17, 22
  - oxygen functional groups Ch 11, 18, 19, 20
- Reduction
  - hydride reduction Ch 8, 10, 11, 17, 18, 19, 20, 21
  - hydrogenation Ch 8, 9, 17, 18, 19
  - metals Ch 9, 17, 18, 19

NEW! Visual **Guides to Organic Reactions** place the reactions covered in each chapter within the overall context of the reactions covered in the course.

The Keys to Organic Chemistry

Over 80 Mechanism Boxes help students understand how specific reactions occur by zooming in on each individual step in detail.

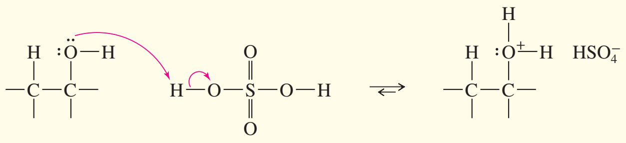
KEY MECHANISM 7-5 Acid-Catalyzed Dehydration of an Alcohol

PROBLEM-SOLVING HINT

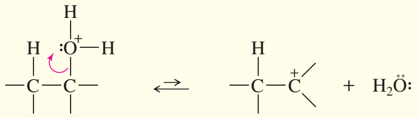
In acid-catalyzed mechanisms, the first step is often addition of H^+, and the last step is often loss of H^+.

Alcohol dehydrations usually involve E1 elimination of the protonated alcohol.

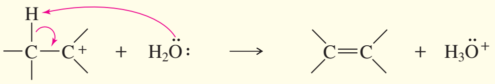
Step 1: Protonation of the hydroxy group (fast equilibrium).



Step 2: Ionization to a carbocation (slow; rate limiting).

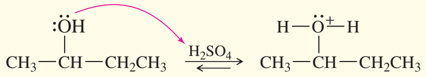


Step 3: Deprotonation to give the alkene (fast).

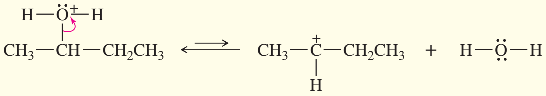


EXAMPLE: Acid-catalyzed dehydration of butan-2-ol

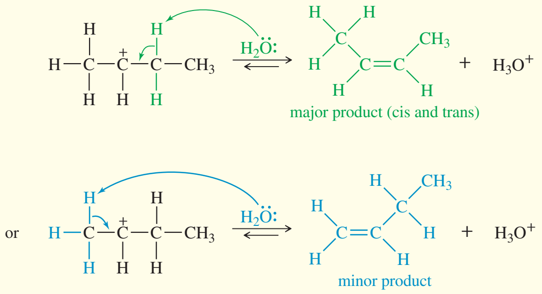
Step 1: Protonation of the hydroxy group (fast equilibrium).



Step 2: Ionization to a carbocation (slow; rate limiting).



Step 3: Deprotonation to give the alkene (fast).



18 Key Mechanism Boxes highlight the fundamental mechanistic principles that recur throughout the course and are the components of many of the longer, more complex mechanisms. Each describes the steps of the reaction in detail with a specific example to reinforce the mechanism and a concluding problem to help students absorb these essential reactions.

NEW! Explanations and Annotations to Mechanisms help students better understand how each mechanism works.

NEW! Over 100 New Problems include more synthesis problems and problems based on recent research literature.

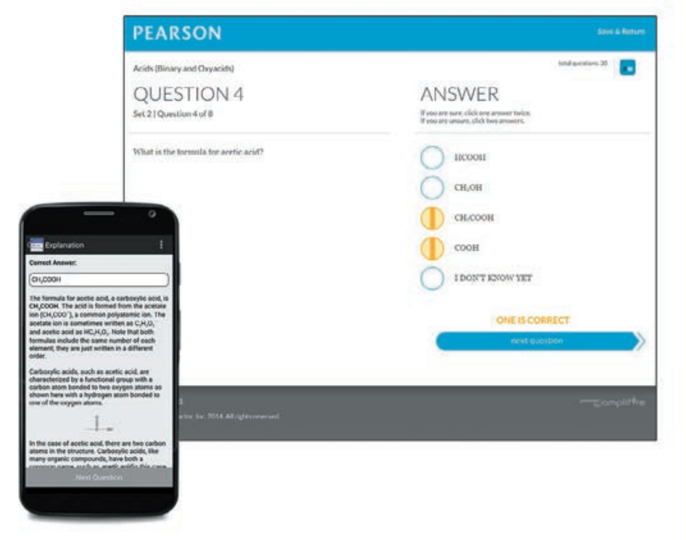
Principles, Preparation, and Problem Solving

MasteringChemistry® www.masteringchemistry.com

MasteringChemistry motivates students to practice organic chemistry outside of class and arrive prepared for lecture. The textbook works with MasteringChemistry to guide students toward what they need to know before testing them on the content. This edition continually engages students through pre-lecture, during-, and post-lecture activities that all include real-life applications.

Dynamic Study Modules

Help students understand the concepts more quickly! Now assignable, Dynamic Study Modules enable your students to study on their own and be better prepared with the fundamental concepts needed from general chemistry, as well as the problem solving skills and practice with nomenclature, functional groups, and key mechanisms skills needed to succeed in the organic chemistry course. The mobile app is available for iOS and Android devices for study on the go, and results can be tracked in the MasteringChemistry gradebook.



Acids (Binary and Oxyacids)

Total questions: 30

QUESTION 4

Set 2 | Question 4 of 8

What is the formula for acetic acid?

ANSWER

If you are sure, click one answer twice.
If you are unsure, click two answers.

○ HCOOH
○ CH_3OH
◐ CH_3COOH
◐ COOH
○ I DON'T KNOW YET

ONE IS CORRECT

Correct Answer:

CH_3COOH

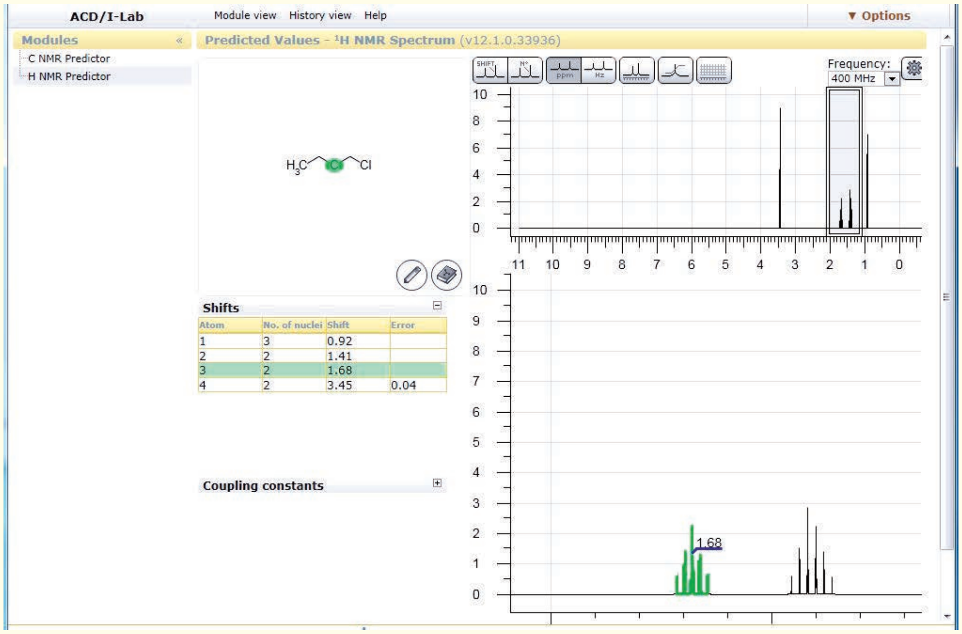
The formula for acetic acid, a carboxylic acid, is CH_3COOH. The acid is formed from the acetate ion (CH_3COO^-), a common polyatomic ion. The acetate ion is sometimes written as $C_2H_3O_2$, and acetic acid as $HC_2H_3O_2$. Note that both formulas include the same number of each element; they are just written in a different order.

Carboxylic acids, such as acetic acid, are characterized by a functional group with a carbon atom bonded to two oxygen atoms as shown here with a hydrogen atom bonded to one of the oxygen atoms.

In the case of acetic acid, there are two carbon atoms in the structure. Carboxylic acids, like many organic compounds, have both a

Spectroscopy Simulations

NEW! Six NMR/IR Spectroscopy simulations (a partnership with ACD labs) allow professors and students access to limitless spectral analysis with guided activities that can be used in lab, in the classroom, or after class to study how spectral information correlates with molecular structures. Activities authored by Mike Huggins, University of West Florida, prompt students to use the spectral simulator to solve analytical problems by drawing the right conclusions from the spectra and combining the NMR and IR data to propose a molecular structure.



Shifts

Atom	No. of nuclei	Shift	Error
1	3	0.92	
2	2	1.41	
3	2	1.68	
4	2	3.45	0.04

Resources in Print and Online

Supplement	Available in Print?	Available Online?	Instructor or Student Supplement	Description
MasteringChemistry®		✓	Instructor and Student Supplement	MasteringChemistry New! Organic Chemistry Dynamic Study modules help students efficiently prepare for lecture and exams by reinforcing understanding of general chemistry prerequisites, acid-base chemistry, functional groups, nomenclature, and key mechanisms. At the end of each personalized question set, Dynamic Study Modules provide feedback on whether the answer submitted was correct and give students an explanation of the correct and incorrect answers. The process repeats until the students answer all of the questions correctly and confidently. (Available at www.masteringchemistry.com)
Solutions Manual by Jan William Simek	✓		Instructor and Student Supplement	This Solutions Manual provides detailed solutions to all in-chapter as well as the end-of-chapter exercises in the text. It is now printed in two-color format to highlight details in the solutions and to improve consistency with the text.
Instructor Resources		✓	Instructor Supplement	This website provides an integrated collection of online resources to help instructors make efficient and effective use of their time. It includes all artwork from the text, including figures and tables in PDF format for high-resolution printing, as well as four pre-built PowerPoint™ presentations. The first presentation contains the images embedded within PowerPoint slides. The second includes a complete lecture outline that is modifiable by the user. Also available are powerpoints of the parent text "in chapter" sample exercises. It also includes the Test Bank. Access resources through http://www.pearsonhighered.com/.
Testbank		✓	Instructor Supplement	This testbank contains over 3000 multiple-choice, true/false, and matching questions. It is available in print format, in the TestGen program, in Word format, and is included in the item library of MasteringChemistry.
Organic Molecular Kit (Darling)	✓		Instructor and Student Supplement	Darling Models™ contain various pieces used to build atoms, bonds, and molecules. This model kit allows you to build molecules and see the three-dimensional aspects of organic chemistry that can only be imagined in a two-dimensional drawing.
Prentice Hall Molecular Model Kit for Organic Chemistry	✓		Instructor and Student Supplement	The Prentice Hall molecular model set allows you to build space-filling and ball-and-stick models of organic molecules. The components are precision-tooled from quality plastics, are virtually indestructible, and come in a sturdy plastic case for easy storage. Provides a useful Instruction Book—with photos, diagrams, and concise discussions of chemical principles.

Acknowledgments

I am pleased to thank the many talented people who helped with this revision. Certainly the largest contribution has come from Jan William Simek, long-time author of the Solutions Manual and now contributing author for this textbook. Jan has provided excellent advice and sound judgment through several editions of the book. In this edition, Jan has authored numerous new and revised sections, developed over 100 new problems, constructed the starburst reaction summaries, and authored the new Nomenclature Appendix.

Jan and I would also like to thank the many reviewers for their valuable insight and commentary. Although we did not adopt all their suggestions, we adopted most of them; they were helpful and contributed to the quality of the final product.

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Finally, we want to thank the people at Pearson, whose dedication and commitment contributed to the completion of this project. Particular thanks are due to Developmental Editor David Chelton, who made thousands of useful suggestions throughout the writing and revision process, and who helped to shape this new edition. Special thanks are also due to Editor-in-Chief Jeanne Zalesky, who guided the project from start to finish and made many useful comments and suggestions that guided the direction of the revision. Director of Development Jennifer Hart and Program Manager Lisa Pierce kept the project moving and ensured the needed resources were made available. Project Managers Elisa Mandelbaum and Heidi Aguiar, and Text and Image Research Lead Maya Gomez kept the production process organized, on track, and on schedule. It has been a pleasure working with all these thoroughly professional and competent people.

We have enjoyed working on this new edition, and we hope that it is a scientific and pedagogical improvement over the eighth edition. We've tried to make this book as error-free as possible, but some errors may have slipped by. If you find errors, or have suggestions about how the book might be improved, please send those errors and suggestions to me at my e-mail address: wadelg@whitman.edu. Errors can be fixed quickly in the next printing. Please send any errors you find in the Solutions Manual, or suggestions for improvements, to Jan Simek at his e-mail address: jsimek@calpoly.edu.

We've already started a file of possible changes and improvements for the next edition, and we hope that many of the current users will contribute suggestions to this file. We hope this book makes the instructor's job easier and helps more students to succeed. That's the most important reason that we continue to work at improving it.

L. G. Wade, Jr.
Walla Walla, Washington
Jan William Simek
San Luis Obispo, California

1

Structure and Bonding

Goals for Chapter 1

1 Review concepts from general chemistry that are essential for success in organic chemistry, such as the electronic structure of the atom, Lewis structures and the octet rule, types of bonding, electronegativity, and formal charges.

2 Predict patterns of covalent and ionic bonding involving C, H, O, N, and the halogens.

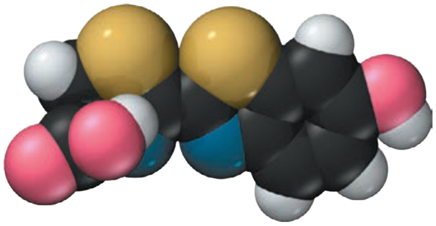
3 Identify resonance-stabilized structures and compare the relative importance of their resonance forms.

4 Draw and interpret the types of structural formulas commonly used in organic chemistry, including condensed structural formulas and line–angle formulas.

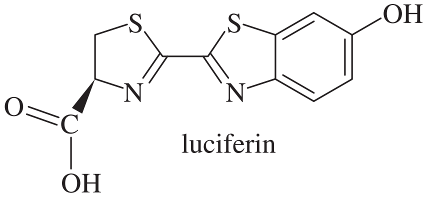
5 Predict the hybridization and geometry of organic molecules based on their bonding.

6 Identify isomers and explain the differences between them.

◀ **Luciferin** is the light-emitting compound found in many firefly (Lampyridae) species. Luciferin reacts with atmospheric oxygen, under the control of an enzyme, to emit the yellow light that fireflies use to attract mates or prey.



luciferin



luciferin

1-1 The Origins of Organic Chemistry

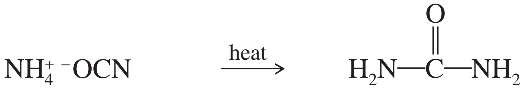
The modern definition of organic chemistry is *the chemistry of carbon compounds*. What is so special about carbon that a whole branch of chemistry is devoted to its compounds? Unlike most other elements, carbon forms strong bonds to other carbon atoms and to a wide variety of other elements. Chains and rings of carbon atoms can be built up to form an endless variety of molecules. This diversity of carbon compounds provides the basis for life on Earth. Living creatures are composed largely of complex organic compounds that serve structural, chemical, or genetic functions.

The term **organic** literally means "derived from living organisms." Originally, the science of organic chemistry was the study of compounds extracted from living organisms and their natural products. Compounds such as sugar, urea, starch, waxes, and plant oils were considered "organic," and people accepted **vitalism,** the belief that natural products needed a "vital force" to create them. Organic chemistry, then, was the study of compounds having the vital force. Inorganic chemistry was the study of gases, rocks, and minerals, and the compounds that could be made from them.

Application: Drug Research

One of the reasons chemists synthesize derivatives of complex organic compounds such as morphine (shown below) is to discover new drugs that retain the good properties (potent pain-relieving) but not the bad properties (highly addictive).

In the 19th century, experiments showed that organic compounds could be synthesized from inorganic compounds. In 1828, the German chemist Friedrich Wöhler converted ammonium cyanate, made from ammonia and cyanic acid, to urea simply by heating it in the absence of oxygen.



$$NH_4^+\ {}^-OCN \xrightarrow{\text{heat}} H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2$$

ammonium cyanate (inorganic) — urea (organic)

Urea had always come from living organisms and was presumed to contain the vital force, yet ammonium cyanate is inorganic and thus lacks the vital force. Some chemists claimed that a trace of vital force from Wöhler's hands must have contaminated the reaction, but most recognized the possibility of synthesizing organic compounds from inorganics. Many other syntheses were carried out, and the vital force theory was eventually discarded.

Because vitalism was disproved in the early 19th century, you'd think it would be extinct by now. And you'd be wrong! Vitalism lives on today in the minds of those who believe that "natural" (plant-derived) vitamins, flavor compounds, etc., are somehow different and more healthful than the identical "artificial" (synthesized) compounds.

As chemists, we know that plant-derived compounds and the synthesized compounds are identical. Assuming they are pure, the only way to tell them apart is through ^{14}C dating: Compounds synthesized from petrochemicals have a lower content of radioactive ^{14}C and appear old because their ^{14}C has decayed over time. Plant-derived compounds are recently synthesized from CO_2 in the air. They have a higher content of radioactive ^{14}C. Some large chemical suppliers provide isotope-ratio analyses to show that their "naturals" have high ^{14}C content and are plant-derived. Such a sophisticated analysis lends a high-tech flavor to this 21st-century form of vitalism.

Even though organic compounds do not need a vital force, they are still distinguished from inorganic compounds. The distinctive feature of organic compounds is that they *all* contain one or more carbon atoms. Still, not all carbon compounds are organic;

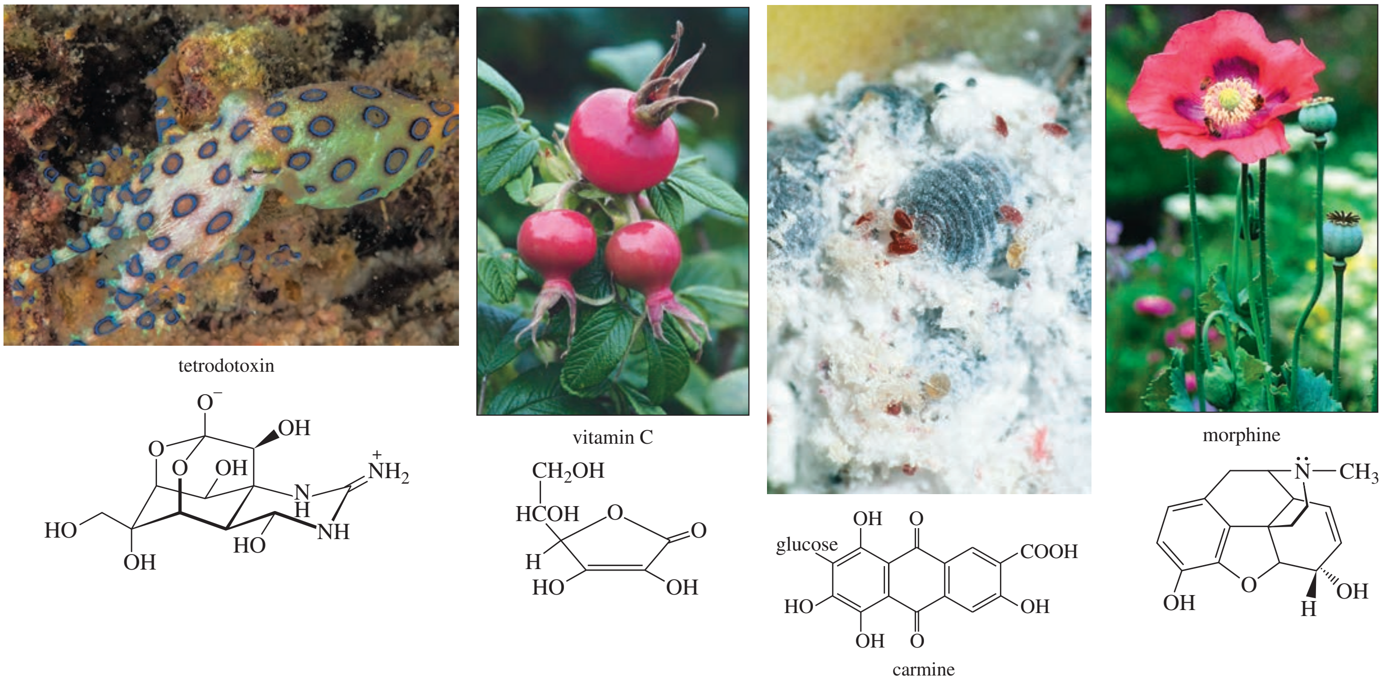


FIGURE 1-1
(a) Venom of the blue-ringed octopus contains tetrodotoxin, which causes paralysis resulting in death. (b) Rose hips contain vitamin C, a radical inhibitor (Chapter 4) that prevents scurvy. (c) The prickly pear cactus is host to cochineal insects, used to prepare the red dye carmine (Chapter 15). (d) Opium poppies contain morphine, an addictive, pain-relieving alkaloid (Chapter 19).

substances such as diamond, graphite, carbon dioxide, ammonium cyanate, and sodium carbonate are derived from minerals and have typical inorganic properties. Most of the millions of carbon compounds are classified as organic, however.

We humans are composed largely of organic molecules, and we are nourished by the organic compounds in our food. The proteins in our skin, the lipids in our cell membranes, the glycogen in our livers, and the DNA in the nuclei of our cells are all organic compounds. Our bodies are also regulated and defended by complex organic compounds.

Chemists have learned to synthesize or simulate many of these complex molecules. The synthetic products serve as drugs, medicines, plastics, pesticides, paints, and fibers. Many of the most important advances in medicine are actually advances in organic chemistry. New synthetic drugs are developed to combat disease, and new polymers are molded to replace failing organs. Organic chemistry has gone full circle. It began as the study of compounds derived from "organs," and now it gives us the drugs and materials we need to save or replace those organs.

The AbioCor® self-contained artificial heart, which is used to sustain patients who are waiting for a heart transplant. The outer shell is polycarbonate, and the valves and inner bladder are polyurethane. Both of these durable substances are synthetic organic compounds.

1-2 Principles of Atomic Structure

Before we begin our study of organic chemistry, we must review some basic principles. These concepts of atomic and molecular structure are crucial to your understanding of the structure and bonding of organic compounds.

1-2A Structure of the Atom

Atoms are made up of protons, neutrons, and electrons. Protons are positively charged and are found together with (uncharged) neutrons in the nucleus. Electrons, which have a negative charge that is equal in magnitude to the positive charge on the proton, occupy the space surrounding the nucleus (Figure 1-2). Protons and neutrons have similar masses, about 1800 times the mass of an electron. Almost all the atom's mass is in the nucleus, but it is the electrons that take part in chemical bonding and reactions.

Each element is distinguished by the number of protons in the nucleus (the atomic number). The number of neutrons is usually similar to the number of protons, although the number of neutrons may vary. Atoms with the same number of protons but different numbers of neutrons are called **isotopes.** For example, the most common kind of carbon atom has six protons and six neutrons in its nucleus. Its mass number (the sum of the protons and neutrons) is 12, and we write its symbol as ^{12}C. About 1% of carbon atoms have seven neutrons; the mass number is 13, written ^{13}C. A very small fraction of carbon atoms have eight neutrons and a mass number of 14. The ^{14}C isotope is radioactive, with a half-life (the time it takes for half of the nuclei to decay) of 5730 years. The predictable decay of ^{14}C is used to determine the age of organic materials up to about 50,000 years old.

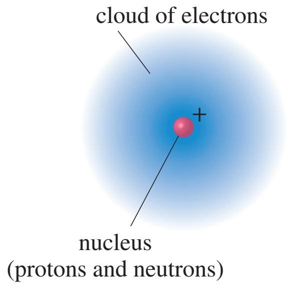
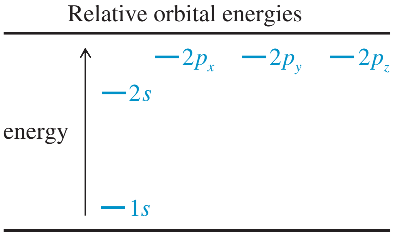


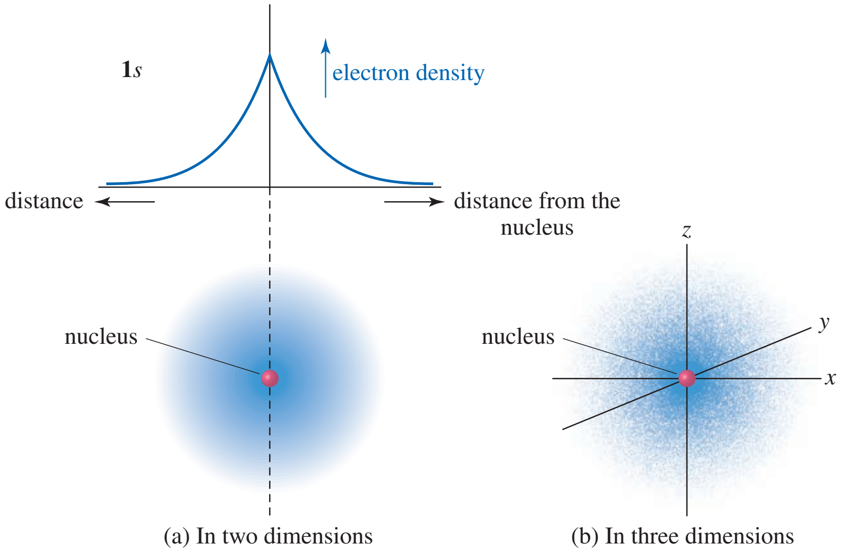
FIGURE 1-2
Basic atomic structure. An atom has a dense, positively charged nucleus surrounded by a cloud of electrons.

1-2B Electron Shells and Orbitals

An element's chemical properties are determined by the number of protons in the nucleus and the corresponding number of electrons around the nucleus. The electrons form bonds and determine the structure of the resulting molecules. Because they are small and light, electrons show properties of both particles and waves; in many ways, the electrons in atoms and molecules behave more like waves than like particles.

Electrons that are bound to nuclei are found in **orbitals.** Orbitals are mathematical descriptions that chemists use to explain and predict the properties of atoms and molecules. The *Heisenberg uncertainty principle* states that we can never determine exactly where the electron is; nevertheless, we can determine the **electron density,** the probability of finding the electron in a particular part of the orbital. An orbital, then, is an allowed energy state for an electron, with an associated probability function that defines the distribution of electron density in space.





(a) In two dimensions (b) In three dimensions

FIGURE 1-3
Graph and diagram of the 1*s* atomic orbital. The electron density is highest at the nucleus and drops off exponentially with increasing distance from the nucleus in any direction.

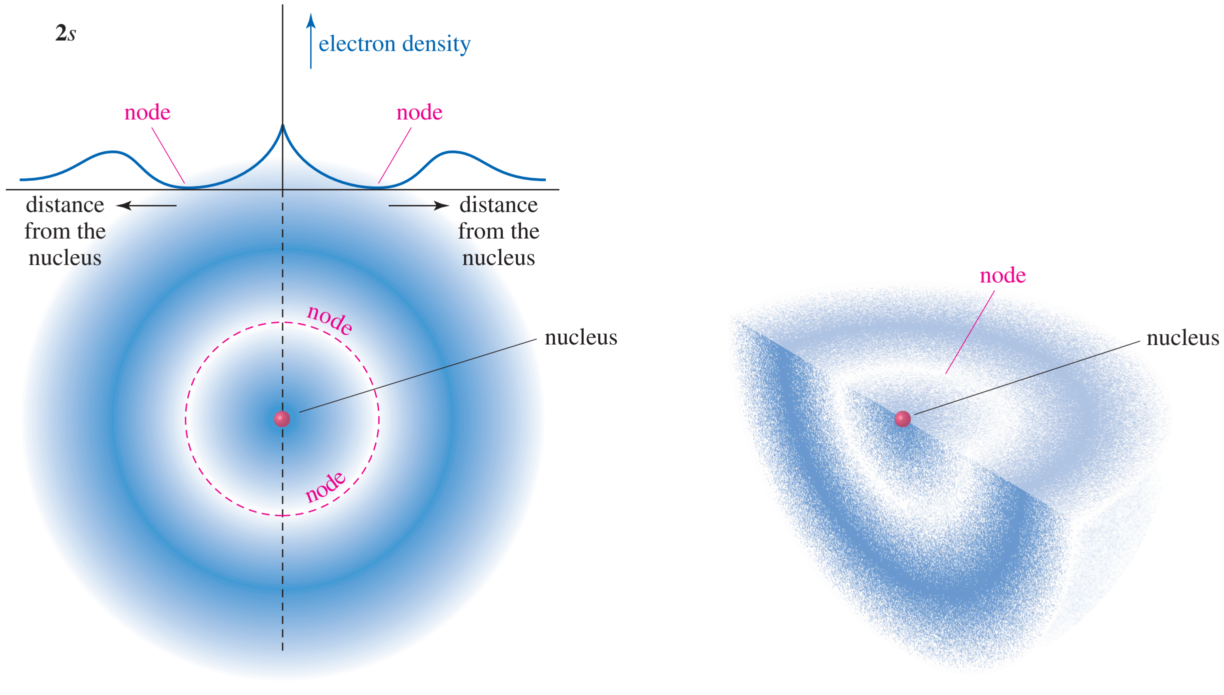
Atomic orbitals are grouped into different "shells" at different distances from the nucleus. Each shell is identified by a principal quantum number n, with $n = 1$ for the lowest-energy shell closest to the nucleus. As n increases, the shells are farther from the nucleus, are higher in energy, and can hold more electrons. Most of the common elements in organic compounds are found in the first two rows of the periodic table, indicating that their electrons are found in the first two electron shells. The first shell ($n = 1$) can hold two electrons, and the second shell ($n = 2$) can hold eight.

The first electron shell contains just the 1*s* orbital. All *s* orbitals are spherically symmetrical, meaning that they are nondirectional. The electron density is only a function of the distance from the nucleus. The electron density of the 1*s* orbital is graphed in Figure 1-3. Notice how the electron density is highest *at* the nucleus and falls off exponentially with increasing distance from the nucleus. The 1*s* orbital might be imagined as a cotton boll, with the cottonseed at the middle representing the nucleus. The density of the cotton is highest nearest the seed, and it becomes less dense at greater distances from this "nucleus."

The second electron shell consists of the 2*s* and 2*p* orbitals. The 2*s* orbital is spherically symmetrical like the 1*s* orbital, but its electron density is not a simple exponential function. The 2*s* orbital has a smaller amount of electron density close to the nucleus. Most of the electron density is farther away, beyond a region of zero electron density called a **node.** Because most of the 2*s* electron density is farther from the nucleus than that of the 1*s*, the 2*s* orbital is higher in energy. Figure 1-4 shows a graph of the 2*s* orbital.

In addition to the 2*s* orbital, the second shell also contains three 2*p* atomic orbitals, one oriented in each of the three spatial directions. These orbitals are called the $2p_x$, the $2p_y$, and the $2p_z$, according to their direction along the x, y, or z axis. The 2*p* orbitals are slightly higher in energy than the 2*s*, because the average location of the electron in a 2*p* orbital is farther from the nucleus. Each *p* orbital consists of two lobes, one on either side of the nucleus, with a **nodal plane** at the nucleus. The nodal plane is a flat (planar) region of space, including the nucleus, with zero electron density. The three 2*p* orbitals differ only in their spatial orientation, so they have identical energies. Orbitals with identical energies are called **degenerate orbitals.** Figure 1-5 shows the shapes of the three degenerate 2*p* atomic orbitals.

The *Pauli exclusion principle* tells us that each orbital can hold a maximum of two electrons, provided that their spins are paired. The first shell (one 1*s* orbital) can accommodate two electrons. The second shell (one 2*s* orbital and three 2*p* orbitals) can accommodate eight electrons, and the third shell (one 3*s* orbital, three 3*p* orbitals, and five 3*d* orbitals) can accommodate 18 electrons.



(a) In two dimensions

(b) In three dimensions (cutaway)

FIGURE 1-4
Graph and diagram of the 2*s* atomic orbital. The 2*s* orbital has a small region of high electron density close to the nucleus, but most of the electron density is farther from the nucleus, beyond a node, or region of zero electron density.

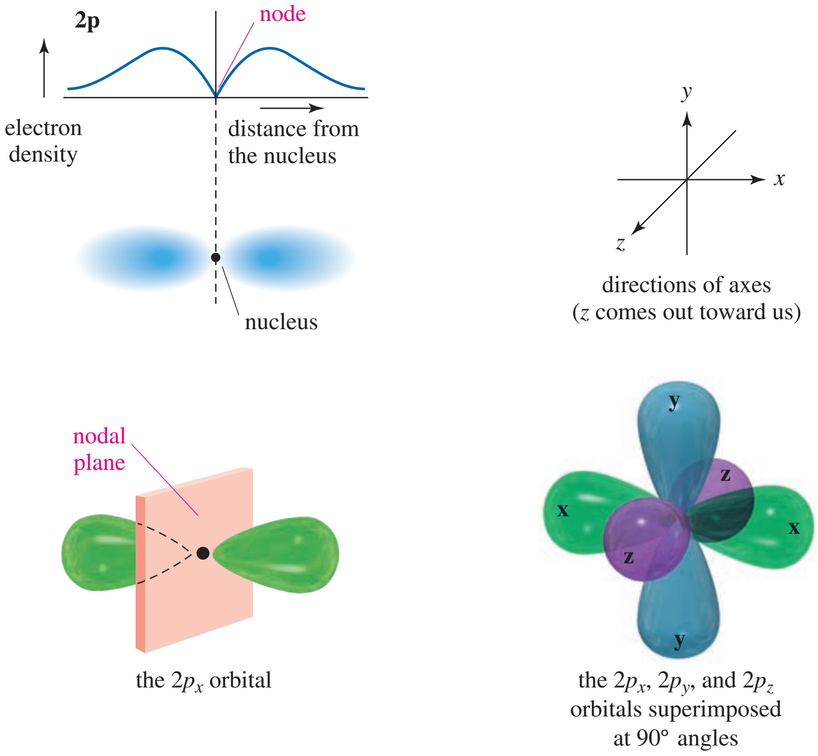


FIGURE 1-5
The 2*p* orbitals. Three 2*p* orbitals are oriented at right angles to each other. Each is labeled according to its orientation along the *x*, *y*, or *z* axis.

Application: Drugs

Lithium carbonate, a salt of lithium, is a mood-stabilizing agent used to treat the psychiatric disorder known as mania. Mania is characterized by behaviors such as elated mood, feelings of greatness, racing thoughts, and an inability to sleep. We don't know how lithium carbonate helps to stabilize these patients' moods.

1-2C Electronic Configurations of Atoms

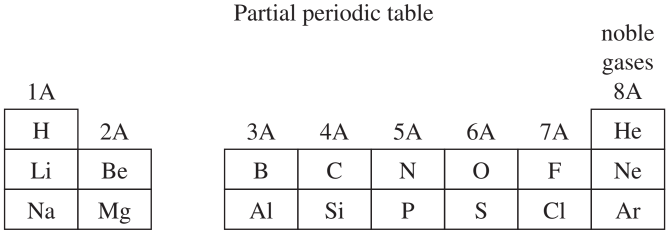
Aufbau means "building up" in German, and the *aufbau principle* tells us how to build up the electronic configuration of an atom's ground (most stable) state. Starting with the lowest-energy orbital, we fill the orbitals in order until we have added the proper number of electrons. Table 1-1 shows the ground-state electronic configurations of the elements in the first two rows of the periodic table.

Two additional concepts are illustrated in Table 1-1. The **valence electrons** are those electrons in the outermost shell. Carbon has four valence electrons, nitrogen has five, and oxygen has six. Helium has a filled first shell with two valence electrons, and neon has has a filled second shell with eight valence electrons (ten electrons total). In general (for the representative elements), the column or group number of the periodic table corresponds to the number of valence electrons (Figure 1-6). Hydrogen and lithium have one valence electron, and they are both in the first column (group 1A) of the periodic table. Carbon has four valence electrons, and it is in group 4A of the periodic table.

Notice in Table 1-1 that carbon's third and fourth valence electrons are not paired; they occupy separate orbitals. Although the Pauli exclusion principle says that two electrons can occupy the same orbital, the electrons repel each other, and pairing requires additional energy. **Hund's rule** states that when there are two or more orbitals of the same energy, electrons go into *different* orbitals rather than pair up in the same orbital. The first 2*p* electron (boron) goes into one 2*p* orbital, the second 2*p* electron (carbon) goes into a different orbital, and the third 2*p* electron (nitrogen) occupies the last 2*p* orbital. The fourth, fifth, and sixth 2*p* electrons must pair up with the first three electrons.

TABLE 1-1
Electronic Configurations of the Elements of the First and Second Rows

Element	Configuration	Valence Electrons
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^22s^1$	1
Be	$1s^22s^2$	2
B	$1s^22s^22p_x^1$	3
C	$1s^22s^22p_x^12p_y^1$	4
N	$1s^22s^22p_x^12p_y^12p_z^1$	5
O	$1s^22s^22p_x^22p_y^12p_z^1$	6
F	$1s^22s^22p_x^2\,2p_y^2\,2p_z^1$	7
Ne	$1s^22s^22p_x^2\,2p_y^2\,2p_z^2$	8



Partial periodic table

1A	2A	3A	4A	5A	6A	7A	noble gases 8A
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

FIGURE 1-6
First three rows of the periodic table. The organization of the periodic table results from the filling of atomic orbitals in order of increasing energy. For these representative elements, the number of the column corresponds to the number of valence electrons.

PROBLEM 1-1

(a) Nitrogen has relatively stable isotopes (half-life greater than 1 second) of mass numbers 13, 14, 15, 16, and 17. (All except ^{14}N and ^{15}N are radioactive.) Calculate how many protons and neutrons are in each of these isotopes of nitrogen.
(b) Write the electronic configurations of the third-row elements shown in the partial periodic table in Figure 1-6.

1-3 Bond Formation: The Octet Rule

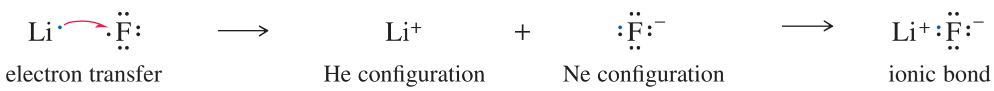
In 1915, G. N. Lewis proposed several new theories describing how atoms bond together to form molecules. One of these theories states that a filled shell of electrons is especially stable, and *atoms transfer or share electrons in such a way as to attain a filled shell of electrons*. A filled shell of electrons is simply the electron configuration of a noble gas, such as He, Ne, or Ar. This principle has come to be called the **octet rule** because a filled shell implies eight valence electrons for the elements in the second row of the periodic table. Elements in the third and higher rows (such as Al, Si, P, S, Cl, and above) can have an "expanded octet" of more than eight electrons because they have low-lying *d* orbitals available.

PROBLEM-SOLVING HINT

When we speak of a molecule having "all octets satisfied," we mean that all the second-row elements have octets. Hydrogen atoms have just two electrons (the He configuration) in their filled valence shell.

1-3A Ionic Bonding

There are two ways that atoms can interact to attain noble-gas configurations. Sometimes atoms attain noble-gas configurations by transferring electrons from one atom to another. For example, lithium has one electron more than the helium configuration, and fluorine has one electron less than the neon configuration. Lithium easily loses its valence electron, and fluorine easily gains one:



A transfer of one electron gives each of these two elements a noble-gas configuration. The resulting ions have opposite charges, and they attract each other to form an **ionic bond.** Ionic bonding usually results in the formation of a large crystal lattice rather than individual molecules. Ionic bonding is common in inorganic compounds but relatively uncommon in organic compounds.

1-3B Covalent Bonding

Covalent bonding, in which electrons are shared rather than transferred, is the most common type of bonding in organic compounds. Hydrogen, for example, needs a second electron to achieve the noble-gas configuration of helium. If two hydrogen atoms come together and form a bond, they "share" their two electrons, and each atom has two electrons in its valence shell.

$$H\cdot \quad + \quad H\cdot \quad \longrightarrow \quad \underset{\text{covalent bond}}{H:H}$$

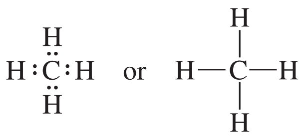
each H shares two electrons
(He configuration)

We will study covalent bonding in more detail later in this chapter.

1-4 Lewis Structures

One way to symbolize the bonding in a covalent molecule is to use **Lewis structures.** In a Lewis structure, each valence electron is symbolized by a dot. A bonding pair of electrons is symbolized by a pair of dots or by a dash (—). We try to arrange all the atoms so that they have their appropriate noble-gas configurations: two electrons for hydrogen, and octets for the second-row elements.

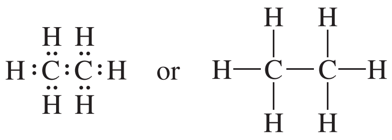
Consider the Lewis structure of methane (CH_4).



methane

Carbon contributes four valence electrons, and each hydrogen contributes one, to give a total of eight electrons. All eight electrons surround carbon to give it an octet, and each hydrogen atom shares two of the electrons with the carbon atom.

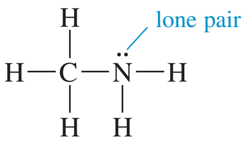
The Lewis structure for ethane (C_2H_6) is more complex.



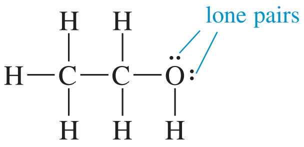
ethane

Once again, we have computed the total number of valence electrons (14) and distributed them so that each carbon atom is surrounded by 8 and each hydrogen by 2. The only possible structure for ethane is the one shown, with the two carbon atoms sharing a pair of electrons and each hydrogen atom sharing a pair with one of the carbons. The ethane structure shows the most important characteristic of carbon—its ability to form strong carbon–carbon bonds.

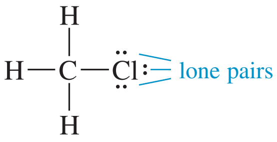
Nonbonding electrons are valence-shell electrons that are *not* shared between two atoms. A pair of nonbonding electrons is often called a **lone pair.** Oxygen atoms, nitrogen atoms, and the halogens (F, Cl, Br, I) usually have nonbonding electrons in their stable compounds. These lone pairs of nonbonding electrons often serve as reactive sites in their parent compounds. The following Lewis structures show one lone pair of electrons on the nitrogen atom of methylamine and two lone pairs on the oxygen atom of ethanol. Halogen atoms usually have three lone pairs, as shown in the structure of chloromethane.



methylamine



ethanol



chloromethane

A correct Lewis structure should show any lone pairs. Organic chemists often draw structures that omit most or all of the lone pairs. These are not true Lewis structures because you must imagine the correct number of nonbonding electrons.

PROBLEM-SOLVING HINT

Lewis structures are the way we write organic chemistry. Learning how to draw them quickly and correctly will help you throughout this course.

PROBLEM 1-2

Draw Lewis structures for the following compounds.

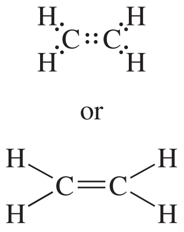
(a) ammonia, NH_3
(b) water, H_2O
(c) hydronium ion, H_3O^+
(d) propane, C_3H_8
(e) dimethylamine, CH_3NHCH_3
(f) diethyl ether, $CH_3CH_2OCH_2CH_3$
(g) 1-chloropropane, $CH_3CH_2CH_2Cl$
(h) propan-2-ol, $CH_3CH(OH)CH_3$
(i) borane, BH_3
(j) boron trifluoride, BF_3

Explain what is unusual about the bonding in the compounds in parts (i) and (j).

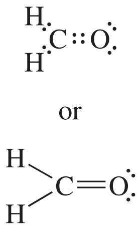
1-5 Multiple Bonding

In drawing Lewis structures in Section 1-4, we placed just one pair of electrons between any two atoms. The sharing of one pair between two atoms is called a **single bond.** Many molecules have adjacent atoms sharing two or even three electron pairs. The sharing of two pairs is called a **double bond,** and the sharing of three pairs is called a **triple bond.**

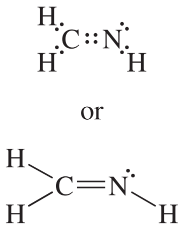
Ethylene (C_2H_4) is an organic compound with a double bond. When we draw a Lewis structure for ethylene, the only way to show both carbon atoms with octets is to draw them sharing two pairs of electrons. The following examples show organic compounds with double bonds. In each case, two atoms share four electrons (two pairs) to give them octets. A double dash (═) symbolizes a double bond.



ethylene

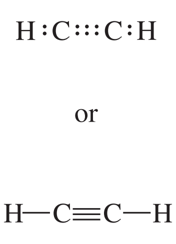


formaldehyde

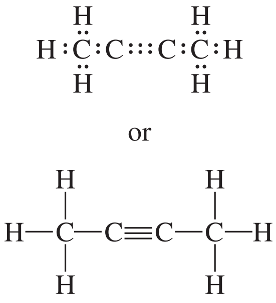


formaldimine

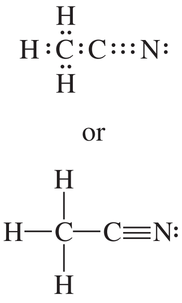
Acetylene (C_2H_2) has a triple bond. Its Lewis structure shows three pairs of electrons between the carbon atoms to give them octets. The following examples show organic compounds with triple bonds. A triple dash (≡) symbolizes a triple bond.



acetylene



dimethylacetylene



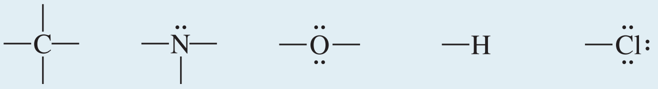
acetonitrile

All these Lewis structures show that carbon normally forms four bonds in neutral organic compounds. Nitrogen generally forms three bonds, and oxygen usually forms two. Hydrogen and the halogens usually form only one bond. The number of bonds an atom usually forms is called its **valence.** Carbon is tetravalent, nitrogen is trivalent, oxygen is divalent, and hydrogen and the halogens are monovalent. By remembering the usual number of bonds for these common elements, we can write organic structures more easily. If we draw a structure with each atom having its usual number of bonds, a correct Lewis structure usually results.

Application: FYI

Acetylene is a high-energy gaseous hydrocarbon that is explosive at high pressures. Combined with oxygen, acetylene burns with such a hot flame that it melts steel. Acetylene is commonly used in welding and cutting torches that work anywhere, even underwater. In gas cylinders, acetylene is dissolved in acetone to keep it from getting too concentrated and exploding.

SUMMARY Common Bonding Patterns (Uncharged)



	carbon	nitrogen	oxygen	hydrogen	halogens
valence:	4	3	2	1	1
lone pairs:	0	1	2	0	3

PROBLEM-SOLVING HINT

These “usual numbers of bonds” might be single bonds, or they might be combined into double and triple bonds. For example, three bonds to nitrogen might be three single bonds, one single bond and one double bond, or one triple bond ($:N\equiv N:$). In working problems, consider all possibilities.

PROBLEM 1-3

Write Lewis structures for the following molecular formulas.

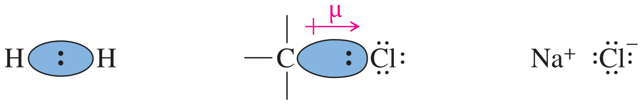
(a) N_2	**(b)** HCN	**(c)** HONO
(d) CO_2	**(e)** CH_3CHNH	**(f)** HCO_2H
(g) C_2H_3Cl	**(h)** HNNH	**(i)** C_3H_6 (one double bond)
(j) C_3H_4 (two double bonds)	**(k)** C_3H_4 (one triple bond)	

PROBLEM 1-4

Circle any lone pairs (pairs of nonbonding electrons) in the structures you drew for Problem 1-3.

1-6 Electronegativity and Bond Polarity

A bond with the electrons shared equally between the two atoms is called a **nonpolar covalent bond.** The bond in H_2 and the C—C bond in ethane are nonpolar covalent bonds. In most bonds between two different elements, the bonding electrons are attracted more strongly to one of the two nuclei. An unequally shared pair of bonding electrons is called a **polar covalent bond.**



nonpolar covalent bond

polar covalent bond

ionic bond

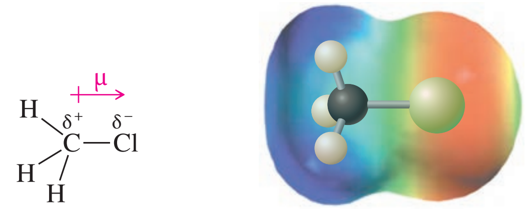
When carbon is bonded to chlorine, for example, the bonding electrons are attracted more strongly to the chlorine atom. The carbon atom bears a small partial positive charge, and the chlorine atom bears a partial negative charge. Figure 1-7 shows the polar carbon–chlorine bond in chloromethane. We symbolize the bond polarity using an arrow with its head at the negative end of the polar bond and a plus sign at the positive end. The bond polarity is measured by its **dipole moment** (μ), defined to be the amount of partial charge (δ^+ and δ^-) multiplied by the bond length (d). The symbol δ^+ means “a small amount of positive charge”; δ^- means “a small amount of negative charge.” To symbolize a dipole moment, we use a crossed arrow pointing from the + charge toward the – charge.

$\mu = \delta \times d$
dipole moment

Figure 1-7 also shows an **electrostatic potential map (EPM)** for chloromethane, using color to represent the calculated charge distribution in the molecule. Red shows electron-rich regions. Blue and purple show electron-poor regions. Orange, yellow, and green show intermediate levels of electrostatic potential. In chloromethane, the red region shows the partial negative charge on chlorine, and the blue region shows the partial positive charges on carbon and the hydrogen atoms.

We often use **electronegativities** as a guide in predicting whether a given bond will be polar and the direction of its dipole moment. The Pauling electronegativity scale, most commonly used by organic chemists, is based on bonding properties, and it is useful for predicting the polarity of covalent bonds. Elements with higher electronegativities generally have more attraction for the bonding electrons. Therefore, in a bond between two different atoms, the atom with the higher electronegativity is the negative end of the dipole. Figure 1-8 shows Pauling electronegativities for some of the important elements in organic compounds.

Notice that the electronegativities increase from left to right across the periodic table. Nitrogen, oxygen, and the halogens are all more electronegative than carbon; sodium, lithium, and magnesium are less electronegative. Hydrogen’s electronegativity is similar to that of carbon, so we usually consider C—H bonds to be nonpolar. We will consider the polarity of bonds and molecules in more detail in Section 2-1.



chloromethane chloromethane

FIGURE 1-7
Bond polarity. Chloromethane contains a polar carbon–chlorine bond with a partial negative charge on chlorine and a partial positive charge on carbon. The electrostatic potential map shows a red region (electron-rich) around the partial negative charge and a blue region (electron-poor) around the partial positive charge. Other colors show intermediate values of electrostatic potential.

H 2.2						
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8						Br 3.0
						I 2.7

FIGURE 1-8
The Pauling electronegativities of some of the elements found in organic compounds.

PROBLEM 1-5

Use electronegativities to predict the direction of the dipole moments of the following bonds.

(a) C—Cl **(b)** C—O **(c)** C—N **(d)** C—S **(e)** C—B
(f) N—Cl **(g)** N—O **(h)** N—S **(i)** N—B **(j)** B—Cl

1-7 Formal Charges

In polar bonds, the partial charges (δ^+ and δ^-) on the bonded atoms are *real*. **Formal charges** provide a method for keeping track of electrons, but they may or may not correspond to real charges. In most cases, if the Lewis structure shows that an atom has a formal charge, it actually bears at least part of that charge. The concept of formal charge helps us determine which atoms bear most of the charge in a charged molecule; it also helps us to see charged atoms in molecules that are neutral overall.

To calculate formal charges, count how many electrons contribute to the charge of each atom and compare that number with the number of valence electrons in the free, neutral atom (given by the group number in the periodic table on the inside back cover). The electrons that contribute to an atom's charge are

1. *all* its unshared (nonbonding) electrons; plus
2. *half* the (bonding) electrons it shares with other atoms, or one electron of each bonding pair.

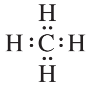
The formal charge of a given atom can be calculated by the formula

$$\text{formal charge (FC)} = [\text{group number}] - [\text{nonbonding electrons}] - \tfrac{1}{2}\,[\text{shared electrons}]$$

SOLVED PROBLEM 1-1

Compute the formal charge (FC) on each atom in the following structures.

(a) Methane (CH_4)



$$\begin{matrix} & \mathrm{H} & \\ \mathrm{H}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & :\mathrm{H} \\ & \mathrm{H} & \end{matrix}$$

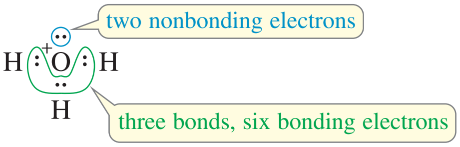
SOLUTION

Each of the hydrogen atoms in methane has one bonding pair of electrons (two shared electrons). Half of two shared electrons is one electron, and one valence electron is what hydrogen needs to be neutral. Hydrogen atoms with one bond are formally neutral: FC $= 1 - 0 - 1 = 0$.

(continued)

The carbon atom has four bonding pairs of electrons (eight electrons). Half of eight shared electrons is four electrons, and four electrons are what carbon (group 4A) needs to be neutral. Carbon is formally neutral whenever it has four bonds: FC $= 4 - 0 - \frac{1}{2}(8) = 0$.

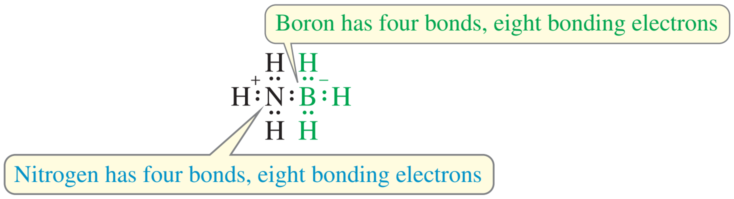
(b) The hydronium ion, H_3O^+



SOLUTION

In drawing the Lewis structure for this ion, we use eight electrons: six from oxygen plus three from the hydrogens, minus one because the ion has a positive charge. Each hydrogen has one bond and is formally neutral. Oxygen is surrounded by an octet, with six bonding electrons and two nonbonding electrons. Half the bonding electrons plus all the nonbonding electrons contribute to its charge: $\frac{6}{2} + 2 = 5$; but oxygen (group 6A) needs six valence electrons to be neutral. Consequently, the oxygen atom has a formal charge of +1: FC $= 6 - 2 - \frac{1}{2}(6) = +1$.

(c) $H_3N{-}BH_3$



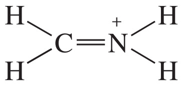
SOLUTION

This is a neutral compound where the individual atoms are formally charged. The Lewis structure shows that both nitrogen and boron have four shared bonding pairs of electrons. Both boron and nitrogen have $\frac{8}{2} = 4$ electrons contributing to their charges. Nitrogen (group 5A) needs five valence electrons to be neutral, so it bears a formal charge of +1. Boron (group 3A) needs only three valence electrons to be neutral, so it bears a formal charge of −1.

Nitrogen: FC $= 5 - 0 - \frac{1}{2}(8) = +1$

Boron: FC $= 3 - 0 - \frac{1}{2}(8) = -1$

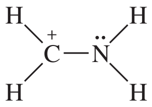
(d) $[H_2CNH_2]^+$



SOLUTION

In this structure, both carbon and nitrogen have four shared pairs of bonding electrons. With four bonds, carbon is formally neutral; however, nitrogen is in group 5A, and it bears a formal positive charge: FC $= 5 - 0 - 4 = +1$.

This compound might also be drawn with the following Lewis structure:



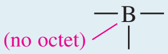
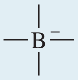
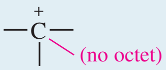
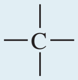
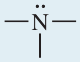
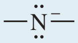
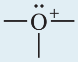
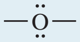
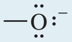
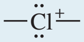
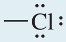
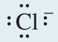
In this structure, the carbon atom has three bonds with six bonding electrons. We calculate that $\frac{6}{2} = 3$ electrons, so carbon is one short of the four needed to be formally neutral: FC $= 4 - 0 - \frac{1}{2}(6) = +1$.

Nitrogen has six bonding electrons and two nonbonding electrons. We calculate that $\frac{6}{2} + 2 = 5$, so the nitrogen is uncharged in this second structure:

$$\text{FC} = 5 - 2 - \tfrac{1}{2}(6) = 0$$

The significance of these two Lewis structures is discussed in Section 1-9.

SUMMARY TABLE 1-1 Common Bonding Patterns in Organic Compounds and Ions

Atom	Valence Electrons	Positively Charged	Neutral	Negatively Charged
B	3			
C	4			
N	5			
O	6			
halogens	7			

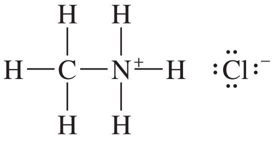
PROBLEM-SOLVING HINT

This is a very important table. Work enough problems to become familiar with these bonding patterns so that you can recognize other patterns as being either unusual or wrong.

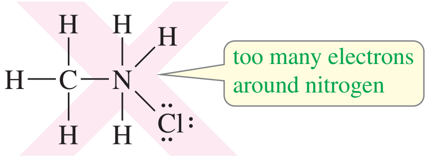
Most organic compounds contain only a few common elements, usually with complete octets of electrons. Summary Table 1-1 shows the most commonly occurring bonding structures, using dashes to represent bonding pairs of electrons. Use the rules for calculating formal charges to verify the charges shown on these structures. A good understanding of the structures shown here will help you to draw organic compounds and their ions quickly and correctly.

1-8 Ionic Structures

Some organic compounds contain ionic bonds. For example, the structure of methylammonium chloride (CH_3NH_3Cl) cannot be drawn using just covalent bonds. That would require nitrogen to have five bonds, implying ten electrons in its valence shell. The correct structure shows the chloride ion ionically bonded to the rest of the structure.

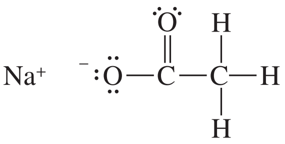


methylammonium chloride

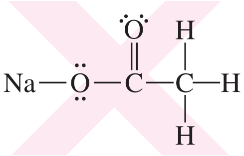


cannot be drawn covalently

Some molecules can be drawn either covalently or ionically. For example, sodium acetate ($NaOCOCH_3$) may be drawn with either a covalent bond or an ionic bond between sodium and oxygen. Because sodium generally forms ionic bonds with oxygen (as in NaOH), the ionically bonded structure is usually preferred. In general, bonds between atoms with very large electronegativity differences (about 2 or more) are usually drawn as ionic.



drawn as ionic
(more common)



drawn as covalent
(less common)

PROBLEM 1-6

Draw Lewis structures for the following compounds and ions, showing appropriate formal charges.

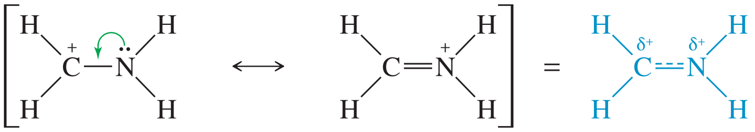
(a) $[CH_3OH_2]^+$
(b) NH_4Cl
(c) $(CH_3)_4NCl$
(d) $NaOCH_3$
(e) $^+CH_3$
(f) $^-CH_3$
(g) $NaBH_4$
(h) $NaBH_3CN$
(i) $(CH_3)_2O{-}BF_3$
(j) $[HONH_3]^+$
(k) $KOC(CH_3)_3$
(l) $[H_2C{=}OH]^+$

1-9 Resonance

Some compounds' structures are not adequately represented by a single Lewis structure. When two or more valence-bond structures are possible, differing only in the placement of electrons, the molecule will usually show characteristics of both structures. The different structures are called **resonance structures** or **resonance forms** because they are not different compounds, just different ways of drawing the same compound. The actual molecule is said to be a **resonance hybrid** of its resonance forms.

1-9A Resonance Hybrids

In Solved Problem 1-1(d), we saw that the ion $[H_2CNH_2]^+$ might be represented by either of the following resonance forms:



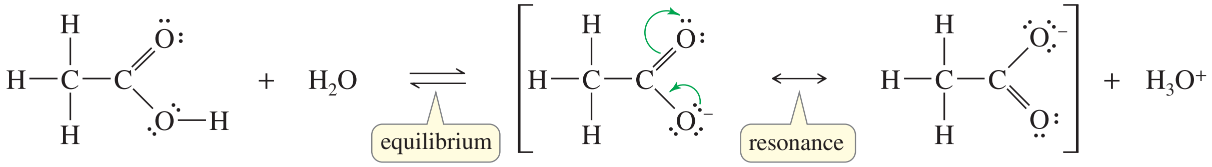
resonance forms of a resonance hybrid

combined representation

The actual structure of this ion is a resonance hybrid of the two structures. In the actual molecule, the positive charge is **delocalized** (spread out) over both the carbon atom and the nitrogen atom. In the left resonance form, the positive charge is on carbon, but carbon does not have an octet. We can imagine moving nitrogen's nonbonding electrons into the bond (as indicated by the green arrow) to give the second structure, with a positive charge on nitrogen and an octet on carbon. The combined representation attempts to combine the two resonance forms into a single picture, with the charge shared by carbon and nitrogen.

Spreading the positive charge over two atoms makes the ion more stable than it would be if the entire charge were localized only on the carbon or only on the nitrogen. We call this a **resonance-stabilized** cation. Resonance is most important when it allows a charge to be delocalized over two or more atoms, as in this example.

Resonance stabilization plays a crucial role in organic chemistry, especially in the chemistry of compounds having double bonds. For example, the acidity of acetic acid (shown below) is enhanced by resonance effects. When acetic acid loses a proton, the resulting acetate ion has a negative charge delocalized over both of the oxygen atoms. Each oxygen atom bears half of the negative charge, and this delocalization stabilizes the ion. Each of the carbon–oxygen bonds is halfway between a single bond and a double bond, and they are said to have a *bond order* of $1\frac{1}{2}$.

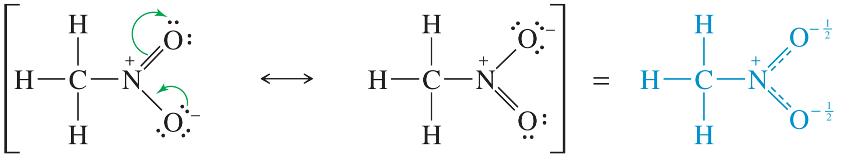


acetic acid

acetate ion

We use a single double-headed arrow between resonance forms (and often enclose them in brackets) to indicate that the actual structure is a hybrid of the Lewis structures we have drawn. By contrast, an equilibrium is represented by two arrows in opposite directions. Occasionally we use curved arrows (shown in green above) to help us see how we mentally move the electrons between one resonance form and another. The electrons do not actually move like these curved arrows show, and they do not “resonate” back and forth. They are delocalized over all the resonance forms at the same time.

Some uncharged molecules actually have resonance-stabilized structures with equal positive and negative formal charges. For example, we can draw two Lewis structures for nitromethane (CH_3NO_2), but both of them have a formal positive charge on nitrogen and a negative charge on one of the oxygens. Thus, nitromethane has a positive charge on the nitrogen atom and a negative charge spread equally over the two oxygen atoms. The N—O bonds are midway between single and double bonds, as indicated in the combined representation:



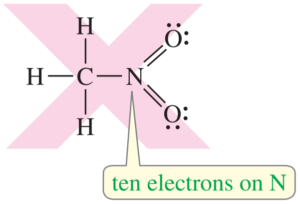
resonance forms

combined representation

Remember that individual resonance forms do not exist. The molecule does not “resonate” between these structures. It is a hybrid with some characteristics of both. An analogy is a mule, which is a hybrid of a horse and a donkey. The mule does not “resonate” between looking like a horse and looking like a donkey; it looks like a mule all the time, with the broad back of the horse and the long ears of the donkey.

PROBLEM-SOLVING HINT

Second-row elements (B, C, N, O, F) cannot have more than eight electrons in their valence shells. The following is NOT a valid Lewis structure:



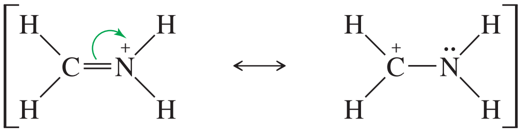
PROBLEM-SOLVING HINT

At this point, we are using four types of arrows in drawing structures and reactions:

- ⟶ Reaction arrows show the reactants converting to products.
- ⇌ Equilibrium arrows show equal rates of the forward and reverse reactions.
- ⟷ Resonance arrows connect forms that are actually the same structure but are drawn with the *delocalized* electrons arranged differently.
- ↶ ∶ Green curved arrows are a mental tool used to imagine moving electrons from one resonance form to another.

1-9B Major and Minor Resonance Contributors

Two or more correct Lewis structures for the same compound may or may not represent electron distributions of equal energy. Although separate resonance forms do not exist, we can estimate their relative energies as if they did exist. More stable resonance forms are closer representations of the real molecule than less stable ones. The two resonance forms shown earlier for the acetate ion have similar bonding, and they are of identical energy. The same is true for the two resonance forms of nitromethane. The following resonance forms are bonded differently, however.

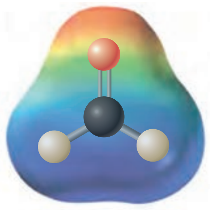


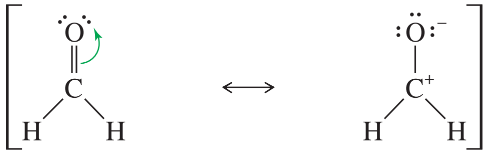
all octets
(major contributor)

no octet on C
(minor contributor)

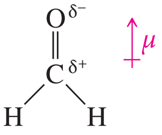
These structures are not equal in estimated energy. The first structure has the positive charge on nitrogen. The second has the positive charge on carbon, and the carbon atom does not have an octet. The first structure is more stable because it has an additional bond and all the atoms have octets. Many stable ions have a positive charge on a nitrogen atom with four bonds (see Summary Table 1-1, page 6). We call the more stable resonance form the **major contributor,** and the less stable form is the **minor contributor.** Lower-energy (more stable) resonance forms are closer representations of the actual molecule or ion than are the higher-energy (less stable) ones.

Many organic molecules have major and minor resonance contributors. Formaldehyde ($H_2C{=}O$) can be written with a negative charge on oxygen, balanced by a positive charge on carbon. This polar resonance form is higher in estimated energy than the double-bonded structure because it has charge separation, fewer bonds, and a positively charged carbon atom without an octet. The charge-separated structure is only a minor contributor, but it helps to explain why the formaldehyde C═O bond is very polar, with a partial positive charge on carbon and a partial negative charge on oxygen. The electrostatic potential map (EPM) of formaldehyde also shows an electron-rich region (red) around oxygen and an electron-poor region (blue) around carbon.


EPM of formaldehyde


all octets
more bonds
no charge separation
(major contributor)

no octet on C
fewer bonds
charge separation
(minor contributor)

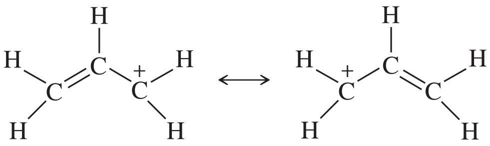


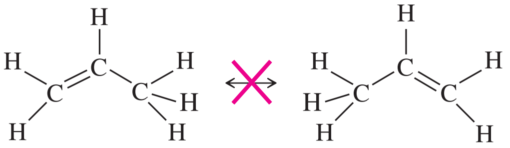
dipole moment

In drawing resonance forms, we try to draw structures that are as low in energy as possible. The best candidates are those that have the maximum number of octets and the maximum number of bonds. Also, we look for structures with the minimum amount of charge separation.

Only electrons can be delocalized. Unlike electrons, nuclei cannot be delocalized. They must remain in the same places, with the same bond distances and angles, in all the resonance contributors. The following general rules will help us to draw realistic resonance structures:

1. All the resonance forms must be valid Lewis structures for the compound. Second-row elements (B, C, N, O, F) can never have more than eight electrons in their valence shells.
2. Only the placement of the electrons may be shifted from one structure to another. Electrons in double bonds and nonbonding electrons (lone pairs) are most commonly shifted.
3. Nuclei cannot be moved, and all bond angles must remain the same.


resonance forms


NOT resonance
a H nucleus has moved

4. Sigma bonds are very stable, and they are rarely involved in resonance.
5. The major resonance contributor is the one with the lowest energy. The best contributors generally have the most octets satisfied, as many bonds as possible, and as little charge separation as possible.
6. Electronegative atoms such as N, O, and halogens often help to delocalize positive charges, but they can bear a positive charge only if they have octets.
7. Resonance stabilization is most important when it serves to delocalize a charge or a radical over two or more atoms.

PROBLEM-SOLVING HINT

Resonance forms can be compared using the following criteria, beginning with the most important:

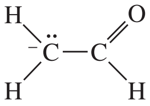
1. As many octets as possible
2. As many bonds as possible
3. As little charge separation as possible
4. Any negative charges on electronegative atoms

SOLVED PROBLEM 1-2

For each of the following compounds, draw the important resonance forms. Indicate which structures are major and minor contributors or whether they would have the same energy.

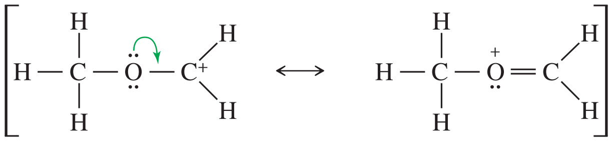
(a) $[CH_3OCH_2]^+$

(b)



(c) H_2SO_4

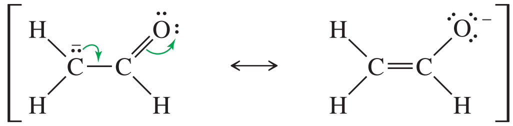
SOLUTION (a)



minor contributor major contributor

The first (minor) structure has a carbon atom with only six electrons around it. The second (major) structure has octets on all atoms and an additional bond.

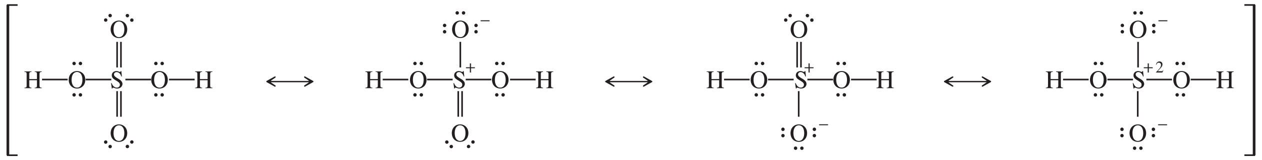
SOLUTION (b)



minor contributor major contributor

Both of these structures have octets on oxygen and both carbon atoms, and they have the same number of bonds. The first structure has the negative charge on carbon; the second has it on oxygen. Oxygen is the more electronegative element, so the second structure is the major contributor.

SOLUTION (c)



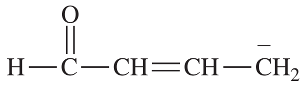
The first structure, with more bonds and less charge separation, is possible because sulfur is a third-row element with accessible *d* orbitals, giving it an expandable valence. For example, SF_6 is a stable compound with 12 electrons around sulfur. Theoretical calculations suggest that the last structure, with octets on all atoms, may be the major resonance contributor, however. Organic chemists mostly draw the first uncharged structure, whereas inorganic chemists mostly prefer the fourth structure with octets on all atoms.

PROBLEM 1-7

Draw the important resonance forms for the following molecules and ions.

(a) CO_3^{2-} **(b)** $H_2C{=}CH{-}\overset{+}{C}H_2$ **(c)** $H_2C{=}CH{-}\overset{-}{C}H_2$ **(d)** NO_3^-

(e) NO_2^- **(f)**



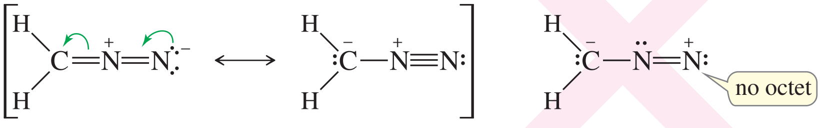
$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}CH{-}\overset{-}{C}H_2$

(g) $[CH_3C(OCH_3)_2\,]^+$ **(h)** $B(OH)_3$

PROBLEM 1-8 (PARTIALLY SOLVED)

For each of the following compounds, draw the important resonance forms. Indicate which structures are major and minor contributors or whether they have the same energy.

(a) H_2CNN



major minor not significant

(continued)

PROBLEM-SOLVING HINT

In drawing resonance forms for ions, see how you can delocalize the charge over several atoms.

Try to spread a negative charge over electronegative elements such as oxygen and nitrogen. Try to spread a positive charge over as many carbons as possible, but especially over any atoms that can bear the positive charge and still have an octet, such as oxygen (with three bonds) or nitrogen (with four bonds).

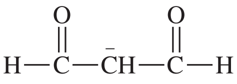
SOLUTION

The first two resonance forms have all their octets satisfied, and they have the same number of bonds. They show that the central nitrogen atom bears a positive charge, and the outer carbon and nitrogen share a negative charge. A nitrogen atom is more electronegative than a carbon atom, so we expect the structure showing the minus charge on nitrogen to be the major contributor.

The third structure is not one we would normally draw, because it is much less significant than the other two. It has a nitrogen atom without an octet, and it has fewer bonds than the other two structures. Nitrogen often bears a positive charge when it has four bonds and an octet, but it rarely bears a positive charge without an octet.

(b) $[H_2CCN]^-$ **(c)** $[H_2COCH_3]^+$ **(d)** $[H_2CNO_2]^-$ **(e)** $[CH_3C(OH)_2]^+$

(f) $[CH_2CHNH]^-$ **(g)**



$$\mathrm{H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{-}{C}H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H}$$

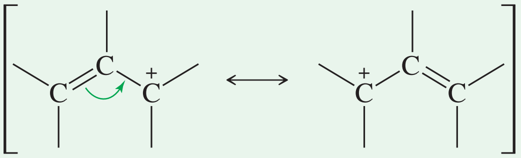
(h) $\mathrm{CHO{-}\bar{C}H{-}CN}$

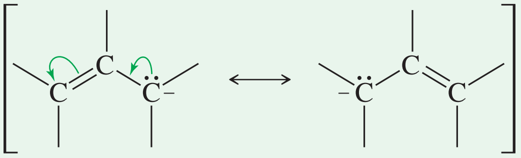
PROBLEM-SOLVING STRATEGY Drawing and Evaluating Resonance Forms

We commonly draw resonance forms (resonance structures) for one of two reasons:

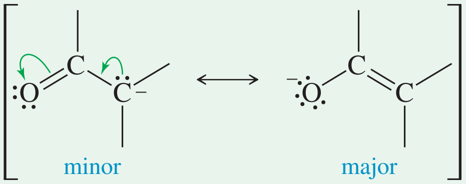
1. To show how delocalization stabilizes a reactive species, such as a cation or anion, by spreading the charge over two or more atoms in a structure.
2. To explain the characteristics of a compound and why it reacts the way it does.

In drawing resonance forms to show how a cation or an anion is delocalized, you should look for double bonds and nonbonding electron pairs (lone pairs) next to the charged atom. A double bond next to a charged atom can delocalize the charge. In drawing resonance forms, you can use curved arrows to keep track of the electrons as you mentally move them from one place to another. Remember that this movement is imaginary. The actual molecule is a mixture of all the resonance forms all the time. The electrons and charges do not move back and forth, but are delocalized throughout the structure.

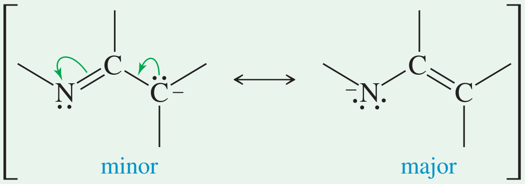




If the double bond allows an electronegative element to share a negative charge, that resonance form will be particularly stable. The most common examples are double bonds to oxygen and nitrogen.



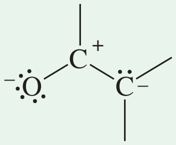
The major resonance form has the negative charge on oxygen, an electronegative element.



The major resonance form has the negative charge on nitrogen, an electronegative element.

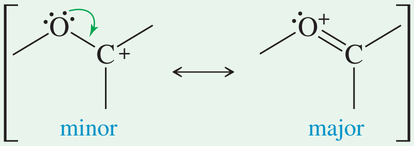
These resonance forms show how the negative charge is spread over a carbon atom and the oxygen or nitrogen atom. All the atoms have octets in both structures, so the more important resonance form is the one with the negative charge on the more electronegative element, either oxygen or nitrogen. Still, these resonance forms show why this anion can react at either the carbon or the oxygen or nitrogen atom.

The resonance form shown below is also a valid Lewis structure, as well as a valid resonance form, but it is not an important resonance form (except in quantum-mechanical calculations) because it does not help to delocalize the negative charge, and it includes unnecessary charge separation and a carbon atom without an octet. You would not draw this resonance form in most cases.

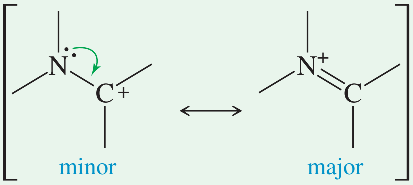


Not an important resonance form. Too much charge separation, too few bonds, and a carbon atom without an octet.

A carbon atom with a positive charge lacks an octet. If it is bonded to an atom with nonbonding electrons (often oxygen or nitrogen), the carbon atom can share those nonbonding electrons. This sharing allows it to gain an octet and delocalize the positive charge onto its neighbor. The following examples show how this delocalization affords more stability to the cation.



The major resonance form has all octets satisfied, and it has more bonds than the other form.



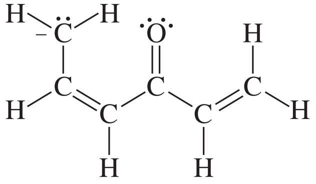
The major resonance form has all octets satisfied, and it has more bonds than the other form.

At first, it seems surprising that the major resonance form has the positive charge on oxygen or nitrogen, which are both more electronegative than carbon. But here, the comparison is between carbon with a positive charge and lacking an octet, versus oxygen or nitrogen with a positive charge and a complete octet. This situation is similar to the stable ions H_3O^+ and NH_4^+, which also bear a positive charge on oxygen or nitrogen, but with a complete octet.

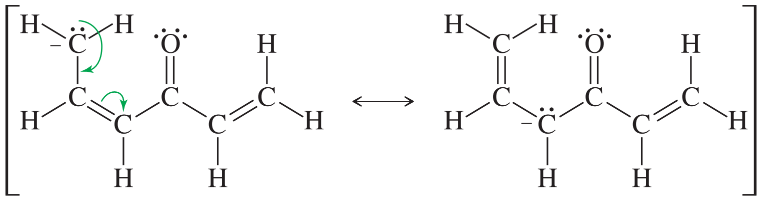
Finally, let's see how you would approach problems that involve delocalizing positive and negative charges.

SOLVED PROBLEM 1-3

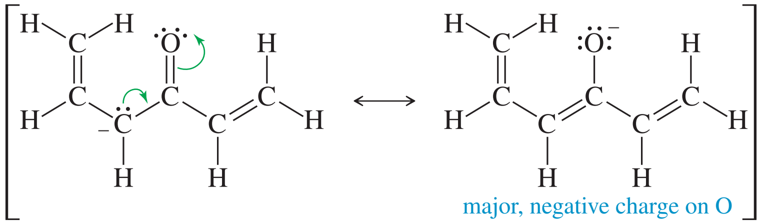
Draw the important resonance forms of the following anion:



Looking ahead, you should try to put the negative charge on the electronegative oxygen atom of the C═O group. But first, the carbon with the negative charge has a C═C double bond next to it. The lone pair can delocalize into the double bond, sharing the negative charge with another carbon.



This second structure now has a C═O double bond next to the carbon bearing the negative charge. Moving the pair of electrons in that direction delocalizes the negative charge onto the oxygen atom, a favorable result.

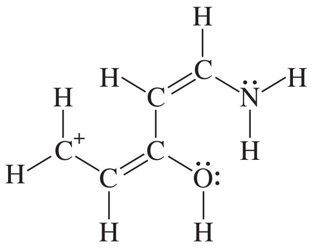


major, negative charge on O

Note that you cannot delocalize the negative charge into the final double bond on the right. There are no valid Lewis structures that place the negative charge on either of these two carbon atoms.

SOLVED PROBLEM 1-4

Draw the important resonance forms of the following cation:



SOLUTION

Looking ahead, you should try to put the positive charge on oxygen (with three bonds) or nitrogen (with four bonds) to give resonance forms with octets. But first, notice the double bond next to the carbon with the positive charge. Moving the electrons in that double bond shares the charge with another carbon. This second carbon has a neighbor (oxygen) with lone pairs that can provide carbon with an octet, giving a relatively stable structure.