

Third Edition

Organic Chemistry

Janice Gorzynski Smith

Periodic Table of the Elements

Group number → 1A

Period number → 1

1	1 H Hydrogen 1.0079
---	-------------------------------------

2A

2	3 Li Lithium 6.941	4 Be Beryllium 9.0122
3	11 Na Sodium 22.9898	12 Mg Magnesium 24.3050

Key			
Atomic number	67	Symbol	Ho
Name	Holmium	Atomic weight	164.9303
An element			



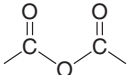
													3A	4A	5A	6A	7A	8A	
													5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984	10 Ne Neon 20.1797	1
													13 Al Aluminum 26.9815	14 Si Silicon 28.0855	15 P Phosphorus 30.9738	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948	2
4	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.9559	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.9380	26 Fe Iron 55.845	27 Co Cobalt 58.9332	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.41	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.9216	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80	4
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.9059	40 Zr Zirconium 91.224	41 Nb Niobium 92.9064	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.82	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.9045	54 Xe Xenon 131.29	5
6	55 Cs Cesium 132.9054	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.2	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.9804	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)	6
7	87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (267)	105 Db Dubnium (268)	106 Sg Seaborgium (271)	107 Bh Bohrium (272)	108 Hs Hassium (270)	109 Mt Meitnerium (276)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (280)	112 — (285)	113 — (284)	114 — (289)	115 — (288)	116 — (293)			7

Lanthanides

Actinides

6	58 Ce Cerium 140.115	59 Pr Praseodymium 140.9076	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.9253	66 Dy Dysprosium 162.50	67 Ho Holmium 164.9303	68 Er Erbium 167.26	69 Tm Thulium 168.9342	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967	6
7	90 Th Thorium 232.0381	91 Pa Protactinium 231.0359	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)	7

COMMON FUNCTIONAL GROUPS

Type of Compound	General Structure	Example	Functional Group	Type of Compound	General Structure	Example	Functional Group
Acid chloride	$\text{R}-\overset{\text{:O:}}{\underset{\text{:Cl:}}{\text{C}}}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{:Cl:}}{\text{C}}}$	$-\text{COCl}$	Aromatic compound			phenyl group
Alcohol	$\text{R}-\ddot{\text{O}}\text{H}$	$\text{CH}_3-\ddot{\text{O}}\text{H}$	$-\text{OH}$ hydroxy group	Carboxylic acid	$\text{R}-\overset{\text{:O:}}{\underset{\text{:O:}}{\text{C}}}-\ddot{\text{O}}\text{H}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{:O:}}{\text{C}}}-\ddot{\text{O}}\text{H}$	$-\text{COOH}$ carboxy group
Aldehyde	$\text{R}-\overset{\text{:O:}}{\underset{\text{H}}{\text{C}}}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{H}}{\text{C}}}$	$\text{C}=\text{O}$ carbonyl group	Ester	$\text{R}-\overset{\text{:O:}}{\underset{\text{:O:R}}{\text{C}}}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{:O:CH}_3}}{\text{C}}$	$-\text{COOR}$
Alkane	$\text{R}-\text{H}$	CH_3CH_3	—	Ether	$\text{R}-\ddot{\text{O}}-\text{R}$	$\text{CH}_3-\ddot{\text{O}}-\text{CH}_3$	$-\text{OR}$ alkoxy group
Alkene	$\text{C}=\text{C}$	$\begin{array}{c} \text{H} & \text{H} \\ & \backslash \text{ } / \\ & \text{C}=\text{C} \\ & / \text{ } \backslash \\ \text{H} & \text{H} \end{array}$	double bond	Ketone	$\text{R}-\overset{\text{:O:}}{\underset{\text{R}}{\text{C}}}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{CH}_3}}{\text{C}}$	$\text{C}=\text{O}$ carbonyl group
Alkyl halide	$\text{R}-\ddot{\text{X}}:$ (X = F, Cl, Br, I)	$\text{CH}_3-\ddot{\text{Br}}:$	$-\text{X}$ halo group	Nitrile	$\text{R}-\text{C}\equiv\text{N:}$	$\text{CH}_3-\text{C}\equiv\text{N:}$	$-\text{C}\equiv\text{N}$ cyano group
Alkyne	$-\text{C}\equiv\text{C}-$	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	triple bond	Sulfide	$\text{R}-\ddot{\text{S}}-\text{R}$	$\text{CH}_3-\ddot{\text{S}}-\text{CH}_3$	$-\text{SR}$ alkylthio group
Amide	$\text{R}-\overset{\text{:O:}}{\underset{\text{H (or R)}}{\underset{\text{H (or R)}}{\text{N}}}}{\text{C}}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{:NH}_2}}{\text{C}}}$	$-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$	Thiol	$\text{R}-\ddot{\text{S}}\text{H}$	$\text{CH}_3-\ddot{\text{S}}\text{H}$	$-\text{SH}$ mercapto group
Amine	$\text{R}-\ddot{\text{N}}\text{H}_2$ or $\text{R}_2\ddot{\text{N}}\text{H}$ or $\text{R}_3\ddot{\text{N}}$	$\text{CH}_3-\ddot{\text{N}}\text{H}_2$	$-\text{NH}_2$ amino group	Thioester	$\text{R}-\overset{\text{:O:}}{\underset{\text{:SR}}{\text{C}}}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{:SCH}_3}}{\text{C}}}$	$-\text{COSR}$
Anhydride	$\text{R}-\overset{\text{:O:}}{\underset{\text{:O:}}{\text{C}}}-\ddot{\text{O}}-\overset{\text{:O:}}{\underset{\text{:O:}}{\text{C}}}-\text{R}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{:O:}}{\text{C}}}-\ddot{\text{O}}-\overset{\text{:O:}}{\underset{\text{:O:}}{\text{C}}}-\text{CH}_3$					

Organic Chemistry

Third Edition

Janice Gorzynski Smith

University of Hawai'i at Mānoa





ORGANIC CHEMISTRY, THIRD EDITION

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*F*or Megan Sarah

About the Author

Janice Gorzynski Smith was born in Schenectady, New York, and grew up following the Yankees, listening to the Beatles, and water skiing on Sacandaga Reservoir. She became interested in chemistry in high school, and went on to major in chemistry at Cornell University where she received an A.B. degree *summa cum laude*. Jan earned a Ph.D. in Organic Chemistry from Harvard University under the direction of Nobel Laureate E. J. Corey, and she also spent a year as a National Science Foundation National Needs Postdoctoral Fellow at Harvard. During her tenure with the Corey group she completed the total synthesis of the plant growth hormone gibberellic acid.

Following her postdoctoral work, Jan joined the faculty of Mount Holyoke College where she was employed for 21 years. During this time she was active in teaching organic chemistry lecture and lab courses, conducting a research program in organic synthesis, and serving as department chair. Her organic chemistry class was named one of Mount Holyoke's "Don't-miss courses" in a survey by *Boston* magazine. After spending two sabbaticals amidst the natural beauty and diversity in Hawai'i in the 1990s, Jan and her family moved there permanently in 2000. She is currently a faculty member at the University of Hawai'i at Mānoa, where she teaches the two-semester organic chemistry lecture and lab courses. In 2003, she received the Chancellor's Citation for Meritorious Teaching.

Jan resides in Hawai'i with her husband Dan, an emergency medicine physician. She has four children: Matthew and Zachary, age 14 (margin photo on page 163); Jenna, a student at Temple University's Beasley School of Law; and Erin, an emergency medicine physician and co-author of the *Student Study Guide/Solutions Manual* for this text. When not teaching, writing, or enjoying her family, Jan bikes, hikes, snorkels, and scuba dives in sunny Hawai'i, and time permitting, enjoys travel and Hawaiian quilting.



The author (far right) and her family from the left: husband Dan, and children Zach, Erin, Jenna, and Matt.

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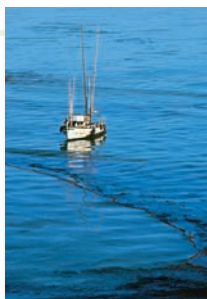
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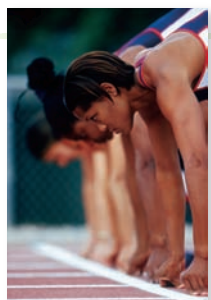
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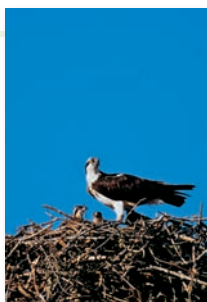
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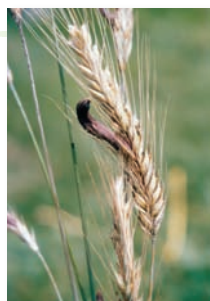
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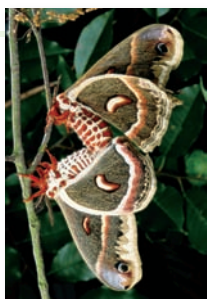
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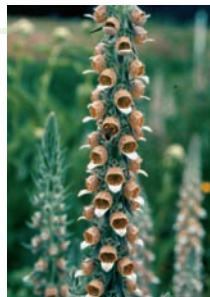
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Preface

My goal in writing *Organic Chemistry* was to create a text that showed students the beauty and logic of organic chemistry by giving them a book that they would *use*. This text is based on lecture notes and handouts that were developed in my own organic chemistry courses over my 30-year teaching career. I have followed two guiding principles: use relevant and interesting applications to illustrate chemical phenomena, and present the material in a student-friendly fashion using bulleted lists, solved problems, and extensive illustrations and summaries. *Organic Chemistry* is my attempt to simplify and clarify a course that intimidates many students—to make organic chemistry interesting, relevant, and accessible to *all* students, both chemistry majors and those interested in pursuing careers in biology, medicine, and other disciplines, without sacrificing the rigor they need to be successful in the future.

The Basic Features

- **Style** This text is different—by design. Today’s students rely more heavily on visual imagery to learn than ever before. The text uses less prose and more diagrams, equations, tables, and bulleted summaries to introduce and reinforce the major concepts and themes of organic chemistry.
- **Content** *Organic Chemistry* accents basic themes in an effort to keep memorization at a minimum. Relevant examples from everyday life are used to illustrate concepts, and this material is integrated throughout the chapter rather than confined to a boxed reading. Each topic is broken down into small chunks of information that are more manageable and easily learned. Sample problems are used as a tool to illustrate stepwise problem solving. Exceptions to the rule and older, less useful reactions are omitted to focus attention on the basic themes.
- **Organization** *Organic Chemistry* uses functional groups as the framework within which chemical reactions are discussed. Thus, the emphasis is placed on the reactions that different functional groups undergo, not on the reactions that prepare them. Moreover, similar reactions are grouped together so that parallels can be emphasized. These include acid–base reactions (Chapter 2), oxidation and reduction (Chapters 12 and 20), radical reactions (Chapter 15), and reactions of organometallic reagents (Chapter 20).

By introducing one new concept at a time, keeping the basic themes in focus, and breaking complex problems down into small pieces, I have found that many students find organic chemistry an intense but learnable subject. Many, in fact, end the year-long course surprised that they have actually *enjoyed* their organic chemistry experience.

Organization and Presentation

For the most part, the overall order of topics in the text is consistent with the way most instructors currently teach organic chemistry. There are, however, some important differences in the way topics are presented to make the material logical and more accessible. This can especially be seen in the following areas.

- **Review material** Chapter 1 presents a healthy dose of review material covering Lewis structures, molecular geometry and hybridization, bond polarity, and types of bonding. While many of these topics are covered in general chemistry courses, they are presented here from an organic chemist’s perspective. I have found that giving students a firm grasp of these fundamental concepts helps tremendously in their understanding of later material.
- **Acids and bases** Chapter 2 on acids and bases serves two purposes. It gives students experience with curved arrow notation using some familiar proton transfer reactions. It also illustrates how some fundamental concepts in organic structure affect a reaction, in this case an acid–base reaction. Since many mechanisms involve one or more acid–base reactions, I emphasize proton transfer reactions early and come back to this topic often throughout the text.

- **Functional groups** Chapter 3 uses the functional groups to introduce important properties of organic chemistry. Relevant examples—PCBs, vitamins, soap, and the cell membrane—illustrate basic solubility concepts. In this way, practical topics that are sometimes found in the last few chapters of an organic chemistry text (and thus often omitted because instructors run out of time) are introduced early so that students can better grasp why they are studying the discipline.
- **Stereochemistry** Stereochemistry (the three-dimensional structure of molecules) is introduced early (Chapter 5) and reinforced often, so students have every opportunity to learn and understand a crucial concept in modern chemical research, drug design, and synthesis.
- **Modern reactions** While there is no shortage of new chemical reactions to present in an organic chemistry text, I have chosen to concentrate on new methods that introduce a particular three-dimensional arrangement in a molecule, so-called asymmetric or enantioselective reactions. Examples include Sharpless epoxidation (Chapter 12), CBS reduction (Chapter 20), and enantioselective synthesis of amino acids (Chapter 28).
- **Grouping reactions** Since certain types of reactions have their own unique characteristics and terminology that make them different from the basic organic reactions, I have grouped these reactions together in individual chapters. These include acid–base reactions (Chapter 2), oxidation and reduction (Chapters 12 and 20), radical reactions (Chapter 15), and reactions of organometallic reagents (Chapter 20). I have found that focusing on a group of reactions that share a common theme helps students to better see their similarities.
- **Synthesis** Synthesis, one of the most difficult topics for a beginning organic student to master, is introduced in small doses, beginning in Chapter 7 and augmented with a detailed discussion of retrosynthetic analysis in Chapter 11. In later chapters, special attention is given to the retrosynthetic analysis of compounds prepared by carbon–carbon bond-forming reactions (for example, Sections 20.11 and 21.10C).
- **Spectroscopy** Since spectroscopy is such a powerful tool for structure determination, four methods are discussed over two chapters (Chapters 13 and 14).
- **Key Concepts** End-of-chapter summaries succinctly summarize the main concepts and themes of the chapter, making them ideal for review prior to working the end-of-chapter problems or taking an exam.

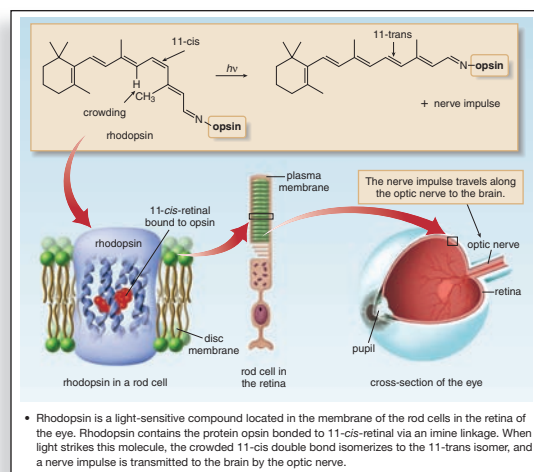
New to the Third Edition

- In response to reviewer feedback, **new sections** have been added on fragmentation patterns in mass spectrometry (Section 13.3) and peptide sequencing (Section 28.6). In addition, sections on splitting in NMR spectroscopy (Section 14.7) and substituent effects in substituted benzenes (Section 18.6) **have been rewritten** to clarify and focus the material. Some **mechanisms have been modified** by adding electron pairs to nucleophiles and leaving groups to more clearly indicate the course of the chemical reaction.
- **Twenty new NMR spectra** have been added in Chapters 14–25 to give students additional practice in this important type of analysis.
- Over **350 new problems** are included in the third edition. The majority of these problems are written at the intermediate level—more advanced than the easier drill problems, but not as complex as the challenge problems. Beginning with Chapter 11, there are additional multi-step synthesis problems that rely on reactions learned in earlier chapters.
- The **interior design has been modified** to tidy margins, and **art labeling has been simplified**, so students can focus more clearly on the important concepts in a section.
- **New micro-to-macro illustrations** are included on hydrogen bonding in DNA (Chapter 3), the production of ethanol from corn (Chapter 9), partial hydrogenation of vegetable oils (Chapter 12), artificial sweeteners (Chapter 27), and insulin (Chapter 28). Several 3-D illustrations of proteins have been added to Chapter 28 as well. The depiction of enzymes as biological catalysts in Chapter 6 has been redone to use an actual reaction—the conversion of the lactose in milk to glucose and galactose.
- **New health-related and environmental applications** are included in margin notes and problems. Topics include the health benefits of omega-3 fatty acids, α -hydroxy acids in skin care products, drugs such as Benadryl that contain ammonium salts, chloroethane as a local anesthetic, rebaudioside A (trade name Truvia), a sweetening agent isolated from a plant source, and many others.

Tools to Make Learning Organic Chemistry Easier

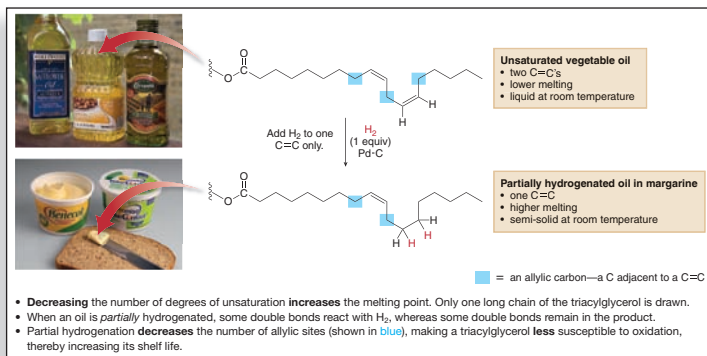
Illustrations

Organic Chemistry is supported by a well-developed illustration program. Besides traditional skeletal (line) structures and condensed formulas, there are numerous ball-and-stick molecular models and electrostatic potential maps to help students grasp the three-dimensional structure of molecules (including stereochemistry) and to better understand the distribution of electronic charge.



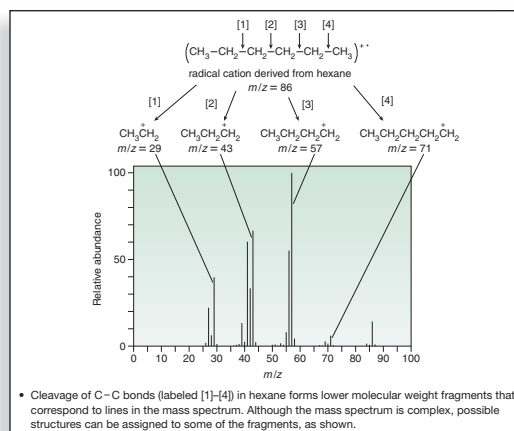
Micro-to-Macro Illustrations

Unique to *Organic Chemistry* are micro-to-macro illustrations, where line art and photos combine with chemical structures to reveal the underlying molecular structures giving rise to macroscopic properties of common phenomena. Examples include starch and cellulose (Chapter 5), adrenaline (Chapter 7), partial hydrogenation of vegetable oil (Chapter 12), and dopamine (Chapter 25).



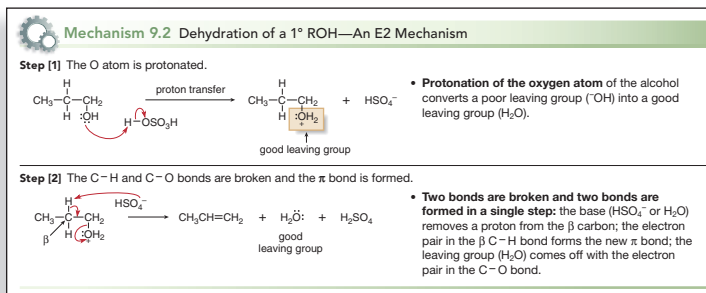
Spectra

Over 100 spectra created specifically for *Organic Chemistry* are presented throughout the text. The spectra are color-coded by type and generously labeled. Mass spectra are green; infrared spectra are red; and proton and carbon nuclear magnetic resonance spectra are blue.



Mechanisms

Curved arrow notation is used extensively to help students follow the movement of electrons in reactions. Where appropriate, mechanisms are presented in parts to promote a better conceptual understanding.



Problem Solving

Sample Problems

Sample Problems show students how to solve organic chemistry problems in a logical, stepwise manner. More than 800 follow-up problems are located throughout the chapters to test whether students understand concepts covered in the Sample Problems.

How To's

How To's provide students with detailed instructions on how to work through key processes.

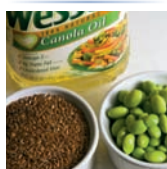
Applications and Summaries

Key Concept Summaries

Succinct summary tables reinforcing important principles and concepts are provided at the end of each chapter.

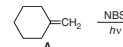
Margin Notes

Margin notes are placed carefully throughout the chapters, providing interesting information relating to topics covered in the text. Some margin notes are illustrated with photos to make the chemistry more relevant.



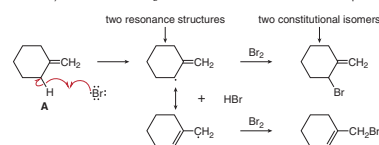
Canola, soybeans, and flaxseed are excellent dietary sources of linolenic acid, an essential fatty acid. Oils derived from omega-3 fatty acids (Problem 10.12) are currently thought to be especially beneficial for individuals at risk of developing coronary artery disease.

Sample Problem 15.4 Draw the products formed when **A** is treated with NBS + $h\nu$.



Solution

Hydrogen abstraction at the allylic C forms a resonance-stabilized radical (with two different resonance structures) that reacts with Br_2 to form two constitutional isomers as products.

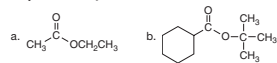


Problem 15.20 Draw all constitutional isomers formed when each alkene is treated with NBS + $h\nu$.

- a. $\text{CH}_3\text{CH}=\text{CHCH}_3$ b. c. $\text{CH}_2=\text{C}(\text{CH}_2\text{CH}_3)_2$

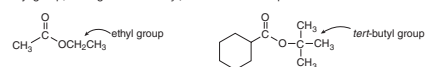
HOW TO Name an Ester ($\text{RCO}_2\text{R}'$) Using the IUPAC System

Example Give a systematic name for each ester:



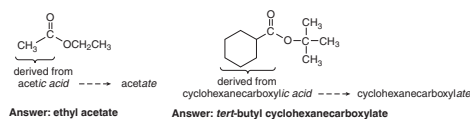
Step [1] Name the R' group bonded to the oxygen atom as an alkyl group.

- The name of the alkyl group, ending in the suffix -yl, becomes the *first* part of the ester name.



Step [2] Name the acyl group ($\text{RCO}-$) by changing the -ic acid ending of the parent carboxylic acid to the suffix -ate.

- The name of the acyl group becomes the *second* part of the name.



KEY CONCEPTS

Alkenes

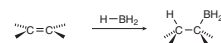
General Facts About Alkenes

- Alkenes contain a carbon-carbon double bond consisting of a stronger σ bond and a weaker π bond. Each carbon is sp^2 hybridized and trigonal planar (10.1).
- Alkenes are named using the suffix **-ene** (10.3).
- Alkenes with different groups on each end of the double bond exist as a pair of diastereomers, identified by the prefixes *E* and *Z* (10.3B).
- Alkenes have weak intermolecular forces, giving them low mp's and bp's, and making them water insoluble. A *cis* alkene is more polar than a *trans* alkene, giving it a slightly higher boiling point (10.4).
- Because a π bond is electron rich and much weaker than a σ bond, alkenes undergo addition reactions with electrophiles (10.8).

Stereochemistry of Alkene Addition Reactions (10.8)

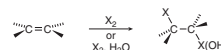
A reagent XY adds to a double bond in one of three different ways:

- Syn addition**— X and Y add from the same side.



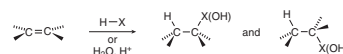
- Syn addition occurs in **hydroboration**.

- Anti addition**— X and Y add from opposite sides.



- Anti addition occurs in **halogenation** and **halohydrin formation**.

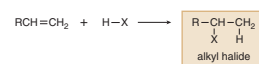
- Both syn and anti addition** occur when carbocations are intermediates.



- Syn and anti addition occur in **hydrohalogenation** and **hydration**.

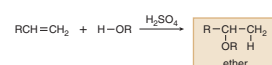
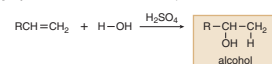
Addition Reactions of Alkenes

[1] Hydrohalogenation—Addition of HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (10.9–10.11)



- The mechanism has two steps.
- Carbocations are formed as intermediates.
- Carbocation rearrangements are possible.
- Markovnikov's rule is followed. H bonds to the less substituted C to form the more stable carbocation.
- Syn and anti addition occur.

[2] Hydration and related reactions (Addition of H_2O or ROH) (10.12)



- For both reactions:
- The mechanism has three steps.
 - Carbocations are formed as intermediates.
 - Carbocation rearrangements are possible.
 - Markovnikov's rule is followed. H bonds to the less substituted C to form the more stable carbocation.
 - Syn and anti addition occur.

Supplements for the Instructor and Student

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Brownstone's Diploma testing software serves up over 1,200 test questions to accompany *Organic Chemistry*. Diploma's software allows you to quickly create a customized test using McGraw-Hill's supplied questions, or by authoring your own questions. Diploma is a downloadable application that allows you to create your tests without an Internet connection—just download the software and question files directly to your computer.

Student Study Guide/Solutions Manual Written by Janice Gorzynski Smith and Erin Smith Berk, the Student Study Guide/Solutions Manual provides step-by-step solutions to all in-chapter and end-of-chapter problems. Each chapter begins with an overview of key concepts and includes key rules and summary tables.

Acknowledgments

When I started working on the first edition of *Organic Chemistry* in the fall of 1999, I had no sense of the magnitude of the task, or any idea of just how many people I would rely upon to complete it. Fortunately, I have had the steadfast support of a dedicated team of publishing professionals at McGraw-Hill.

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Although every effort has been made to make this text and its accompanying Student Study Guide/Solutions Manual as error-free as possible, some errors undoubtedly remain and for them, I am solely responsible. Please feel free to email me about any inaccuracies, so that subsequent editions may be further improved.

With much aloha,

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List of *How To*'s

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List of Selected Applications

Applications make any subject seem more relevant and interesting—for nonmajors and majors alike. The following is a list of the most important biological, medicinal, and environmental applications that have been integrated throughout *Organic Chemistry*. Each chapter opener showcases a current application relating to the chapter's topic. (Code: G = general; M = medicinal; B = biological; E = environmental)

Prologue

- G, E Examples of simple organic compounds—methane, a component in natural gas; ethanol, the alcohol in beer and wine; and trichlorofluoromethane, a refrigerant and aerosol propellant implicated in ozone destruction
- M Some complex organic compounds that are useful drugs—the antibiotic amoxicillin, the antidepressant fluoxetine (Prozac), and AZT, a drug used to treat HIV
- B Ginkgolide B, principal component of extracts from the ginkgo tree, *Ginkgo biloba*

Chapter 1 Structure and Bonding

- M L-Dopa, the drug of choice for the treatment of Parkinson's disease (Opener, Section 1.13)
- M Fosamax, a drug used to prevent bone loss in women (Section 1.4B)

Chapter 2 Acids and Bases

- M The acid–base chemistry of aspirin, the most widely used over-the-counter drug (Opener, Section 2.7)
- M Pseudoephedrine, the nasal decongestant in Sudafed (Section 2.5, Problem 2.18)

Chapter 3 Introduction to Organic Molecules and Functional Groups

- B Vitamin C, a water-soluble vitamin needed in the formation of the protein collagen (Opener)
- B How geckos stick to walls and ceilings (Section 3.3B)
- E Solubility principles and the pollutants MTBE and PCBs in the environment (Section 3.4C)
- B How structure explains the fat solubility of vitamin A and the water solubility of vitamin C (Section 3.5)
- G How soap cleans away dirt (Section 3.6)
- B The structure of the cell membrane (Section 3.7A)
- M How ionophores like the antibiotic valinomycin transport ions across a cell membrane (Section 3.7B)
- B Hydrogen bonding in DNA, deoxyribonucleic acid, the high molecular weight compound that stores the genetic information of an organism (Section 3.9)

Chapter 4 Alkanes

- G Alkanes, the major constituents of petroleum, which is refined to produce gasoline, diesel fuel, and home heating oil (Opener, Section 4.7)
- E The combustion of alkanes, the concentration of atmospheric carbon dioxide, and global warming (Section 4.14B)
- B An introduction to lipids, biomolecules whose properties can be explained by understanding alkane chemistry; cholesterol in the cell membrane (Section 4.15)

Chapter 5 Stereochemistry

- M The importance of the three-dimensional structure in the pain reliever (*S*)-naproxen (Opener)
- B How differences in the three-dimensional structure of starch and cellulose affect their shape and function (Section 5.1)
- M The three-dimensional structure of thalidomide, the anti-nausea drug that caused catastrophic birth defects (Section 5.5)
- M How mirror image isomers can have drastically different properties—the analgesic ibuprofen, the antidepressant fluoxetine, and the anti-inflammatory agent naproxen (Section 5.13)
- B The sense of smell—How mirror image isomers can smell differently (Section 5.13)

Chapter 6 Understanding Organic Reactions

- B Energy changes in the metabolism of glucose and the combustion of isooctane, a high-octane component of gasoline (Opener, Section 6.4)
- B Enzymes, biological catalysts (Section 6.11)

Chapter 7 Alkyl Halides and Nucleophilic Substitution

- B The biological synthesis of adrenaline, the hormone secreted in response to a strenuous or challenging activity (Opener, Section 7.12)
- E CFCs and DDT, two polyhalogenated compounds once widely used, now discontinued because of adverse environmental effects (Section 7.4)

- B S-Adenosylmethionine (SAM), a nutritional supplement used by the cell in key nucleophilic substitutions that synthesize amino acids, hormones, and neurotransmitters (Section 7.12)
- B How nitrosamines, compounds formed in cured meats preserved with sodium nitrite, are thought to be cancer-causing (Section 7.16)
- M The importance of organic synthesis in preparing useful drugs such as aspirin and taxol, an anticancer drug used to treat breast cancer (Section 7.19)

Chapter 8 Alkyl Halides and Elimination Reactions

- E DDE, a degradation product of the pesticide DDT (Opener, Section 8.1)
- B, M Elimination reactions in the synthesis of a prostaglandin, an antimalarial drug, and a female sex hormone (Section 8.4)

Chapter 9 Alcohols, Ethers, and Epoxides

- B Palytoxin, a toxic component isolated from marine soft corals of the genus *Palythoa* (Opener, Problem 9.80)
- G, E Ethanol, a gasoline additive and renewable fuel source that can be produced from the fermentation of carbohydrates in grains (Section 9.5)
- M The design of asthma drugs that block the synthesis of leukotrienes, highly potent molecules that contribute to the asthmatic response (Section 9.16)
- B The metabolism of polycyclic aromatic hydrocarbons (PAHs) to carcinogens that disrupt normal cell function resulting in cancer or cell death (Section 9.17)

Chapter 10 Alkenes

- B Fats and oils—the properties of saturated and unsaturated fatty acids (Opener, Section 10.6)
- G Ethylene, the starting material for preparing the polymer polyethylene and many other simple compounds used to make a variety of other polymers (Section 10.5)
- B Omega-3 fatty acids, highly unsaturated fatty acids thought to be beneficial for individuals at risk of developing coronary artery disease (Section 10.6, Problem 10.12)
- B The synthesis of the female sex hormone estrone (Section 10.15B)
- M The synthesis of artemisinin, an antimalarial drug isolated from qinghao, a Chinese herbal remedy (Section 10.16)

Chapter 11 Alkynes

- M Oral contraceptives (Opener, Section 11.4)
- M Synthetic hormones mifepristone and Plan B, drugs that prevent pregnancy (Section 11.4)

Chapter 12 Oxidation and Reduction

- B The metabolism of ethanol, the alcohol in alcoholic beverages (Opener, Section 12.14)
- B The partial hydrogenation of vegetable oils and the formation of “trans fats” (Section 12.4)
- B The use of disparlure, a sex pheromone, in controlling the spread of gypsy moths (Section 12.8)
- G Blood alcohol screening (Section 12.12)
- E Green chemistry—environmentally benign oxidation reactions (Section 12.13)
- B The synthesis of insect pheromones using asymmetric epoxidation (Section 12.15)

Chapter 13 Mass Spectrometry and Infrared Spectroscopy

- M Infrared spectroscopy and the structure determination of penicillin (Opener, Section 13.8)
- M Using instrumental analysis to detect THC, the active component in marijuana, and other drugs (Section 13.4B)
- B Mass spectrometry and high molecular weight biomolecules (Section 13.4C)

Chapter 14 Nuclear Magnetic Resonance Spectroscopy

- M Modern spectroscopic methods and the structure of the hormone melatonin (Opener, Problem 14.26)
- M Magnetic resonance imaging (MRI) and medicine (Section 14.12)

Chapter 15 Radical Reactions

- G Polystyrene, a common synthetic polymer used in packaging materials and beverage cups (Opener)
- E Ozone destruction and CFCs (Section 15.9)
- B The oxidation of unsaturated lipids by radical reactions (Section 15.11)
- M, B Two antioxidants—naturally occurring vitamin E and synthetic BHT (Section 15.12)
- G The formation of useful polymers from monomers by radical reactions (Section 15.14)

Chapter 16 Conjugation, Resonance, and Dienes

- M Lycopene, a highly unsaturated red pigment found in tomatoes, watermelon, and other fruits (Opener, Section 16.7)
- B The Diels–Alder reaction and the synthesis of tetrodotoxin, a toxin isolated from the puffer fish (Section 16.12)
- M The synthesis of steroids by Diels–Alder reactions (Section 16.14C)
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- B, M Capsaicin, the spicy component of hot peppers and active ingredient in topical creams for the treatment of chronic pain (Opener)
- G Polycyclic aromatic hydrocarbons (PAHs), constituents of cigarette smoke and diesel exhaust (Section 17.5)
- M Examples of common drugs that contain an aromatic ring—Zoloft, Valium, Novocain, Viracept, Viagra, and Claritin (Section 17.5)
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- M The synthesis of the hallucinogen LSD (Opener, Section 18.5D)
- M, E Examples of biologically active aryl chlorides—the drugs bupropion and chlorpheniramine, and 2,4-D and 2,4,5-T, herbicide components of the defoliant Agent Orange (Section 18.3)
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- B, M Reduction reactions in the synthesis of the analgesic ibuprofen and the perfume component muscone (Section 20.4)
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- M Digoxin, a naturally occurring drug isolated from the woolly foxglove plant and used to treat congestive heart failure (Opener, Problem 21.40)
- B Naturally occurring cyanohydrin derivatives—linamarin, from cassava root; and amygdalin, often called laetrile, from apricot, peach, and wild cherry pits (Section 21.9B)
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- G Nylon, the first synthetic fiber (Opener)
- M, B Compounds that contain an ester—vitamin C; cocaine, addictive stimulant from the leaves of the coca plant; and FK506, an immunosuppressant (Section 22.6)
- M, B Useful amides—proteins, the polyamide met-enkephalin, the anticancer drug Gleevec, the penicillin antibiotics, and the cephalosporin antibiotics (Section 22.6)
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- M The synthesis of tamoxifen, an anticancer drug used in the treatment of breast cancer (Opener, Section 23.8C)
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- M The synthesis of the anti-inflammatory agent ibuprofen (Opener, Problem 24.19)
- B The synthesis of periplanone B, sex pheromone of the female American cockroach (Section 24.3)
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- M Histamine, antihistamines, and antiulcer drugs like Tagamet (cimetidine) (Section 25.6B)
- B Naturally occurring alkaloids—atropine from the poisonous nightshade plant, nicotine from tobacco, and coniine from hemlock (Section 25.6B)
- B, M Biologically active derivatives of 2-phenylethylamine—adrenaline, noradrenaline, methamphetamine, mescaline, and dopamine (Section 25.6C)
- B, M The neurotransmitter serotonin and widely used antidepressants called SSRIs (selective serotonin reuptake inhibitors) (Section 25.6C)
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- B, E Bombykol, the sex pheromone of the female silkworm moth (Opener, Section 26.2B)
- E Pyrethrin I, a biodegradable insecticide isolated from chrysanthemums (Section 26.4, Problem 26.33)
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- B Glucose, the most common simple sugar (Section 27.6)
- B, M Naturally occurring glycosides—salicin from willow bark and solanine, isolated from the deadly nightshade plant (Section 27.7C)
- G Rebaudioside A (trade name Truvia), a sweet glycoside from the stevia plant (Section 27.7C)
- B Common disaccharides—maltose from malt, lactose from milk, and sucrose, common table sugar (Section 27.12)
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- B, M Glucosamine, an over-the-counter remedy used for osteoarthritis, and chitin, the carbohydrate that gives rigidity to crab shells (Section 27.14A)
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- B Myoglobin, the protein that stores oxygen in tissues (Opener, Section 28.10C)
- B The naturally occurring amino acids (Section 28.1)
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- B Cholesterol, the most prominent steroid (Opener, Section 29.8B)
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- B, M The structure of steroids—cholesterol, female sex hormones, male sex hormones, adrenal cortical steroids, anabolic steroids, and oral contraceptives (Section 29.8)
- M Cholesterol and cholesterol-lowering drugs atorvastatin (Lipitor) and simvastatin (Zocor) (Section 29.8B)

Chapter 30 Synthetic Polymers

- G Polyethylene terephthalate, an easily recycled synthetic polymer used in transparent soft drink containers (Opener, Sections 30.6B and 30.9A)
- G Polyethylene, the plastic in milk jugs and plastic bags, and other chain-growth polymers (Section 30.2)
- G Using Ziegler–Natta catalysts to make high-density polyethylene (Section 30.4)
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Prologue



What is organic chemistry?
Some representative organic
molecules
Ginkgolide B—A complex
organic compound from the
ginkgo tree

Organic chemistry. You might wonder how a discipline that conjures up images of eccentric old scientists working in basement laboratories is relevant to you, a student in the twenty-first century.

Consider for a moment the activities that occupied your past 24 hours. You likely showered with soap, drank a caffeinated beverage, ate at least one form of starch, took some medication, read a newspaper, listened to a CD, and traveled in a vehicle that had rubber tires and was powered by fossil fuels. If you did any *one* of these, your life was touched by organic chemistry.

What Is Organic Chemistry?

- Organic chemistry is the chemistry of compounds that contain the element carbon.

It is one branch in the entire field of chemistry, which encompasses many classical subdisciplines including inorganic, physical, and analytical chemistry, and newer fields such as bioinorganic chemistry, physical biochemistry, polymer chemistry, and materials science.

Organic chemistry was singled out as a separate discipline for historical reasons. Originally, it was thought that compounds in living things, termed **organic compounds**, were fundamentally different from those in nonliving things, called **inorganic compounds**. Although we have known for more than 150 years that this distinction is artificial, the name *organic* persists. Today the term refers to the study of the compounds that contain carbon, many of which, incidentally, are found in living organisms.

It may seem odd that a whole discipline is devoted to the study of a single element in the periodic table, when more than 100 elements exist. It turns out, though, that there are far more organic compounds than any other type. **Organic chemicals affect virtually every facet of our lives, and for this reason, it is important and useful to know something about them.**

Clothes, foods, medicines, gasoline, refrigerants, and soaps are composed almost solely of organic molecules. Some, like cotton, wool, or silk are naturally occurring; that is, they can be isolated directly from natural sources. Others, such as nylon and polyester, are synthetic, meaning they are produced by chemists in the laboratory. By studying the principles and concepts of organic chemistry, you can learn more about compounds such as these and how they affect the world around you.

Realize, too, what organic chemistry has done for us. Organic chemistry has made available both comforts and necessities that were previously nonexistent, or reserved for only the wealthy. We have seen an enormous increase in life span, from 47 years in 1900 to over 70 years currently. To a large extent this is due to the isolation and synthesis of new drugs to fight infections and the availability of vaccines for childhood diseases. Chemistry has also given us the tools to control insect populations that spread disease, and there is more food for all because of fertilizers, pesticides, and herbicides. Our lives would be vastly different today without the many products that result from organic chemistry (Figure 1).

Figure 1

Products of organic chemistry
used in medicine

a. Oral contraceptives



b. Plastic syringes



c. Antibiotics



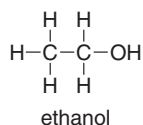
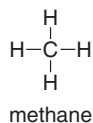
d. Synthetic heart valves



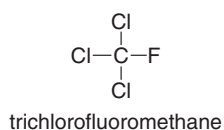
- Organic chemistry has given us contraceptives, plastics, antibiotics, and the knitted material used in synthetic heart valves.

Some Representative Organic Molecules

Perhaps the best way to appreciate the variety of organic molecules is to look at a few. Three simple organic compounds are **methane**, **ethanol**, and **trichlorofluoromethane**.



- Methane**, the simplest of all organic compounds, contains one carbon atom. Methane—the main component of natural gas—occurs widely in nature. Like other hydrocarbons—organic compounds that contain only carbon and hydrogen—**methane is combustible**; that is, it burns in the presence of oxygen. Methane is the product of the anaerobic (without air) decomposition of organic matter by bacteria. The natural gas we use today was formed by the decomposition of organic material millions of years ago. Hydrocarbons such as methane are discussed in Chapter 4.
- Ethanol**, the alcohol present in beer, wine, and other alcoholic beverages, is formed by the fermentation of sugar, quite possibly the oldest example of organic synthesis. Ethanol can also be made in the lab by a totally different process, but **the ethanol produced in the lab**



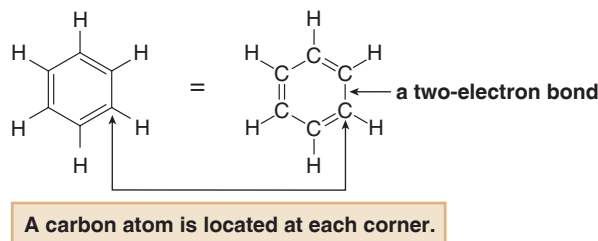
is identical to the ethanol produced by fermentation. Alcohols including ethanol are discussed in Chapter 9.

- **Trichlorofluoromethane** is a member of a class of molecules called **chlorofluorocarbons** or **CFCs**, which contain one or two carbon atoms and several halogens. Trichlorofluoromethane is an unusual organic molecule in that **it contains no hydrogen atoms**. Because it has a low molecular weight and is easily vaporized, trichlorofluoromethane has been used as an aerosol propellant and refrigerant. It and other CFCs have been implicated in the destruction of the stratospheric ozone layer, as is discussed in Chapter 15.

Because more complicated organic compounds contain many carbon atoms, organic chemists have devised a shorthand to draw them. Keep in mind the following when examining these structures:

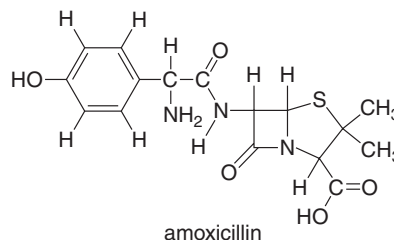
- **Each solid line represents a two-electron covalent bond.**
- **When no atom is drawn at the corner of a ring, an organic chemist assumes it to be carbon.**

For example, in the six-membered ring drawn, there is one carbon atom at each corner of the hexagon.

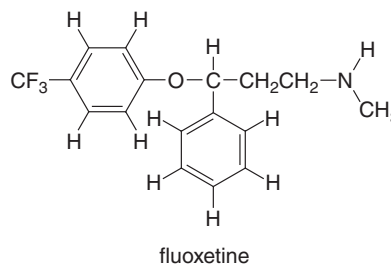


Three complex organic molecules that are important medications are **amoxicillin**, **fluoxetine**, and **AZT**.

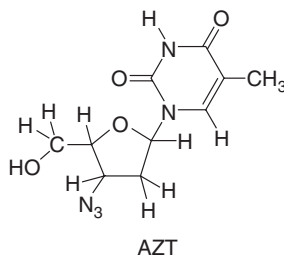
- **Amoxicillin** is one of the most widely used antibiotics in the penicillin family. The discovery and synthesis of such antibiotics in the twentieth century have made routine the treatment of infections that were formerly fatal. You were likely given some amoxicillin to treat an ear infection when you were a child. The penicillin antibiotics are discussed in Chapter 22.



- **Fluoxetine** is the generic name for the antidepressant **Prozac**. Prozac was designed and synthesized by chemists in the laboratory, and is now produced on a large scale in chemical factories. Because it is safe and highly effective in treating depression, Prozac is widely prescribed. Over 40 million individuals worldwide have used Prozac since 1986.

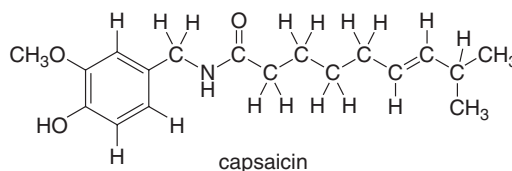


- **AZT**, the abbreviation for **azidodeoxythymidine**, is a drug that treats human immunodeficiency virus (HIV), the virus that causes acquired immune deficiency syndrome (AIDS). Also known by its generic name **zidovudine**, AZT represents a chemical success to a different challenge: synthesizing agents that combat viral infections.

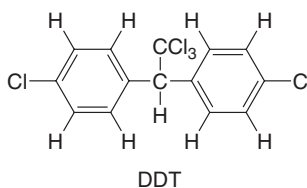


Other complex organic compounds having interesting properties are **capsaicin** and **DDT**.

- **Capsaicin**, one member of a group of compounds called *vanilloids*, is responsible for the characteristic spiciness of hot peppers. It is the active ingredient in pepper sprays used for personal defense and topical creams used for pain relief.



- **DDT**, the abbreviation for **dichlorodiphenyltrichloroethane**, is a pesticide once called “miraculous” by Winston Churchill because of the many lives it saved by killing disease-carrying mosquitoes. DDT use is now banned in the United States and many developed countries because it is a nonspecific insecticide that persists in the environment.



What are the common features of these organic compounds?

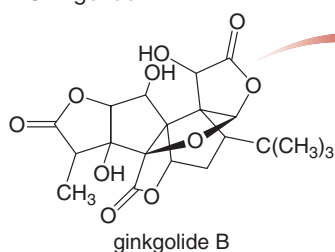
- **All organic compounds contain carbon atoms and most contain hydrogen atoms.**
- **All the carbon atoms have four bonds.** A stable carbon atom is said to be *tetravalent*.
- Other elements may also be present. **Any atom that is not carbon or hydrogen is called a heteroatom.** Common heteroatoms include N, O, S, P, and the halogens.
- Some compounds have **chains** of atoms and some compounds have **rings**.

These features explain why there are so many organic compounds: **Carbon forms four strong bonds with itself and other elements. Carbon atoms combine together to form rings and chains.**

Ginkgolide B—A Complex Organic Compound from the Ginkgo Tree

Let's complete this discussion with **ginkgolide B** ($C_{20}H_{24}O_{10}$), a complex organic compound isolated from the ginkgo tree *Ginkgo biloba*, the oldest seed-producing plant that currently lives on earth (Figure 2). Also called the maidenhair tree, *Ginkgo biloba* has existed for over 280 million years, and fossil records indicate that it has undergone little significant evolutionary change for eons. Extracts from the roots, bark, leaves, and seeds have been used in traditional Chinese

Figure 2
Ginkgolide B



- Hydrogen atoms bonded to ring carbons are omitted in the structure of ginkgolide B, a convention described in Section 1.7.

medicine to treat asthma and improve blood circulation. Today, ginkgo extracts comprise the most widely taken herbal supplements, used by some individuals to enhance memory and treat dementia. Recent findings of the National Institutes of Health, however, have cast doubt on its efficacy in providing any long-term improvement in cognitive function.

In 1932 ginkgolide B was one of four components isolated from ginkgo extracts, and its structure was determined in 1967. Although its rigid ring system of 20 carbons contained in a compact three-dimensional shape made it a challenging molecule to prepare in the laboratory, Professor E. J. Corey and co-workers at Harvard University reported the synthesis of ginkgolide B in the laboratory in 1988.

In this introduction, we have seen a variety of molecules that have diverse structures. They represent a miniscule fraction of the organic compounds currently known and the many thousands that are newly discovered or synthesized each year. The principles you learn in organic chemistry will apply to all of these molecules, from simple ones like methane and ethanol, to complex ones like capsaicin and ginkgolide B. It is these beautiful molecules, their properties, and their reactions that we will study in organic chemistry.

WELCOME TO THE WORLD OF ORGANIC CHEMISTRY!

1

Structure and Bonding

- 1.1 The periodic table
- 1.2 Bonding
- 1.3 Lewis structures
- 1.4 Lewis structures continued
- 1.5 Resonance
- 1.6 Determining molecular shape
- 1.7 Drawing organic structures
- 1.8 Hybridization
- 1.9 Ethane, ethylene, and acetylene
- 1.10 Bond length and bond strength
- 1.11 Electronegativity and bond polarity
- 1.12 Polarity of molecules
- 1.13 L-Dopa—A representative organic molecule



L-Dopa, also called levodopa, was first isolated from seeds of the broad bean plant *Vicia faba* in 1913. Since 1967 it has been the drug of choice for the treatment of Parkinson's disease, a debilitating illness that results from the degeneration of neurons that produce the neurotransmitter dopamine in the brain. L-Dopa is an oral medication that is transported to the brain by the bloodstream, where it is converted to dopamine. Since L-dopa must be taken in large doses with some serious side effects, today it is often given with other drugs that lessen its negative impact on an individual. In Chapter 1, we learn about the structure, bonding, and properties of organic molecules like L-dopa.

Before examining organic molecules in detail, we must review some important features about structure and bonding learned in previous chemistry courses. We will discuss these concepts primarily from an organic chemist's perspective, and spend time on only the particulars needed to understand organic compounds.

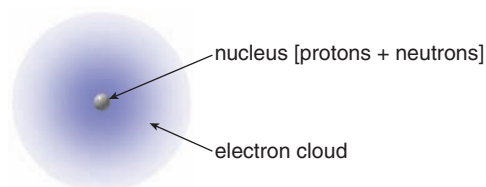
Important topics in Chapter 1 include drawing Lewis structures, predicting the shape of molecules, determining what orbitals are used to form bonds, and how electronegativity affects bond polarity. Equally important is Section 1.7 on drawing organic molecules, both shorthand methods routinely used for simple and complex compounds, as well as three-dimensional representations that allow us to more clearly visualize them.

1.1 The Periodic Table

All matter is composed of the same building blocks called **atoms**. There are two main components of an atom.

- The **nucleus** contains positively charged **protons** and uncharged **neutrons**. Most of the mass of the atom is contained in the nucleus.
- The **electron cloud** is composed of negatively charged **electrons**. The electron cloud comprises most of the volume of the atom.

Schematic of an atom



The charge on a proton is equal in magnitude but opposite in sign to the charge on an electron. In a neutral atom, the **number of protons in the nucleus equals the number of electrons**. This quantity, called the **atomic number**, is unique to a particular element. For example, every neutral carbon atom has an atomic number of six, meaning it has six protons in its nucleus and six electrons surrounding the nucleus.

In addition to neutral atoms, we will also encounter **charged ions**.

- A **cation** is positively charged and has fewer electrons than its neutral form.
- An **anion** is negatively charged and has more electrons than its neutral form.

The number of neutrons in the nucleus of a particular element can vary. **Isotopes** are two atoms of the same element having a different number of neutrons. The **mass number** of an atom is the total number of protons and neutrons in the nucleus. Isotopes have different mass numbers.

Isotopes of carbon and hydrogen are sometimes used in organic chemistry, as we will see in Chapter 14.

- The most common isotope of hydrogen has one proton and no neutrons in the nucleus, but 0.02% of hydrogen atoms have one proton and one neutron. This isotope of hydrogen is called **deuterium**, and is sometimes symbolized by the letter **D**.
- Most carbon atoms have six protons and six neutrons in the nucleus, but 1.1% have six protons and seven neutrons.

The **atomic weight** is the weighted average of the mass of all isotopes of a particular element, reported in atomic mass units (amu).

Each atom is identified by a one- or two-letter abbreviation that is the characteristic symbol for that element. Carbon is identified by the single letter **C**. Sometimes the atomic number is indicated as a subscript to the left of the element symbol, and the mass number is indicated as a superscript, as shown in Figure 1.1.

Figure 1.1

A comparison of two isotopes of the element carbon

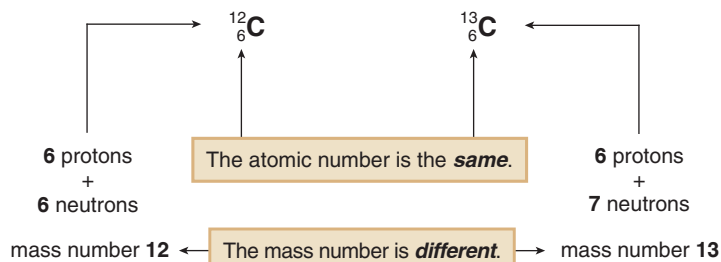


Figure 1.2

A periodic table of the common elements seen in organic chemistry

Diagram illustrating a truncated periodic table with group numbers (1A to 8A) and element symbols. Carbon (C) is located in group 4A, second row.

- Note the location of carbon in the second row, group 4A.

A **row** in the periodic table is also called a **period**, and a **column** is also called a **group**. A periodic table is located on the inside front cover for your reference.

Long ago it was realized that groups of elements have similar properties, and that these atoms could be arranged in a schematic way called the **periodic table**. There are more than 100 known elements, arranged in the periodic table in order of increasing atomic number. The periodic table is composed of rows and columns.

- Elements in the same row are similar in **size**.
- Elements in the same column have similar **electronic and chemical properties**.

Each column in the periodic table is identified by a **group number**, an Arabic (1 to 8) or Roman (I to VIII) numeral followed by the letter A or B. For example, carbon is located in group **4A** in the periodic table in this text.

Carbon's entry in the periodic table:

group number	→ 4A
atomic number	→ 6
element symbol	→ C
element name	→ Carbon
atomic weight	→ 12.011

Although more than 100 elements exist, most are not common in organic compounds. Figure 1.2 contains a truncated periodic table, indicating the handful of elements that are routinely seen in this text. **Most of these elements are located in the first and second rows of the periodic table.**

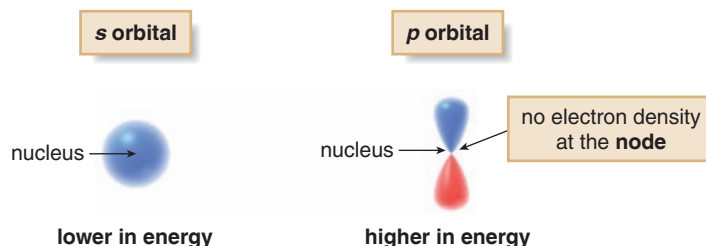
Across each row of the periodic table, electrons are added to a particular shell of orbitals around the nucleus. The shells are numbered 1, 2, 3, and so on. Adding electrons to the first shell forms the first row. Adding electrons to the second shell forms the second row. **Electrons are first added to the shells closest to the nucleus.** These electrons are held most tightly.

Each shell contains a certain number of subshells called **orbitals**. An orbital is a region of space that is high in electron density. There are four different kinds of orbitals, called **s**, **p**, **d**, and **f**. The first shell has only one orbital, called an **s** orbital. The second shell has two kinds of orbitals, **s** and **p**, and so on. Each type of orbital occupies a certain space and has a particular shape.

For the first- and second-row elements, we must deal with only **s orbitals** and **p orbitals**.

- An **s orbital** has a **sphere of electron density**. It is **lower in energy** than other orbitals of the same shell, because electrons are kept close to the positively charged nucleus. An **s** orbital is filled with electrons before a **p** orbital in the same shell.
- A **p orbital** has a **dumbbell shape**. It contains a **node of electron density** at the nucleus. A node means there is no electron density in this region. A **p** orbital is **higher in energy** than

an s orbital (in the same shell) because its electron density is farther away from the nucleus. A p orbital is filled with electrons only after an s orbital of the same shell is full.



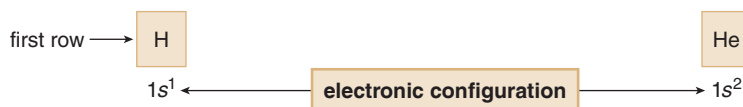
Let's now look at the elements in the first and second rows of the periodic table.

The First Row

The first row of the periodic table is formed by adding electrons to the first shell of orbitals around the nucleus. There is only one orbital in the first shell, called the **1s orbital**.

- **Remember: Each orbital can have a maximum of two electrons.**

As a result, there are **two elements in the first row**, one having one electron added to the 1s orbital, and one having two. The element hydrogen (H) has what is called a $1s^1$ configuration with one electron in the 1s orbital, and helium (He) has a $1s^2$ configuration with two electrons in the 1s orbital.

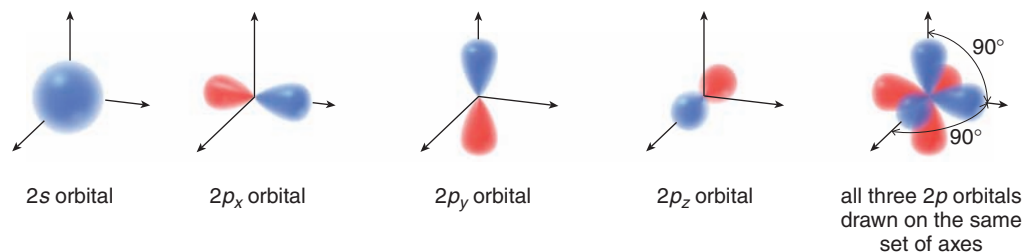


The Second Row

Every element in the second row has a filled first shell of electrons. Thus, all second-row elements have a $1s^2$ configuration. These electrons in the inner shell of orbitals are called **core electrons**, and are not usually involved in the chemistry of a particular element.

Each element in the second row of the periodic table has four orbitals available to accept additional electrons:

- **one 2s orbital**, the s orbital in the second shell
- **three 2p orbitals**, all dumbbell-shaped and perpendicular to each other along the x , y , and z axes



Because each of the four orbitals in the second shell can hold two electrons, there is a **maximum capacity of eight electrons** for elements in the second row. The second row of the periodic table consists of eight elements, obtained by adding electrons to the 2s and three 2p orbitals.

group number	→ 1A	2A					
second row	→ Li	Be					
number of valence electrons	→ 1	2					

	3A	4A	5A	6A	7A	8A
	B	C	N	O	F	Ne
	3	4	5	6	7	8

The outermost electrons are called **valence electrons**. The valence electrons are more loosely held than the electrons closer to the nucleus, and as such, they participate in chemical reactions. **The group number of a second-row element reveals its number of valence electrons.** For example, carbon in group 4A has four valence electrons, and oxygen in group 6A has six.

Problem 1.1 While the most common isotope of nitrogen has a mass number of 14 (nitrogen-14), a radioactive isotope of nitrogen has a mass number of 13 (nitrogen-13). Nitrogen-13 is used in PET (positron emission tomography) scans by physicians to monitor brain activity and diagnose dementia. For each isotope, give the following information: (a) the number of protons; (b) the number of neutrons; (c) the number of electrons in the neutral atom; and (d) the group number.

Problem 1.2 Consider the three atoms: [1] $^{31}_{15}\text{P}$; [2] $^{19}_9\text{F}$; and [3] ^2_1H . For each atom give the following information: (a) the atomic number; (b) the total number of electrons in the neutral atom; (c) the number of valence electrons; and (d) the group number.

1.2 Bonding

Until now our discussion has centered on individual atoms, but it is more common in nature to find two or more atoms joined together.

- **Bonding is the joining of two atoms in a stable arrangement.**

Bonding may occur between atoms of the same or different elements. Bonding is a favorable process because it always leads to **lowered energy and increased stability**. Joining two or more elements forms **compounds**. Although only about 100 elements exist, more than 30 million compounds are known. Examples of compounds include hydrogen gas (H_2), formed by joining two hydrogen atoms, and methane (CH_4), the simplest organic compound, formed by joining a carbon atom with four hydrogen atoms.

One general rule governs the bonding process.

- **Through bonding, atoms attain a complete outer shell of valence electrons.**

Alternatively, because the noble gases in column 8A of the periodic table are especially stable as atoms having a filled shell of valence electrons, the general rule can be restated.

- **Through bonding, atoms attain a stable noble gas configuration of electrons.**

What does this mean for first- and second-row elements? **A first-row element like hydrogen can accommodate two electrons around it.** This would make it like the noble gas helium at the end of the same row. **A second-row element is most stable with eight valence electrons around it** like neon. Elements that behave in this manner are said to follow the **octet rule**.

There are two different kinds of bonding: **ionic bonding** and **covalent bonding**.

- **Ionic bonds result from the transfer of electrons from one element to another.**
- **Covalent bonds result from the sharing of electrons between two nuclei.**

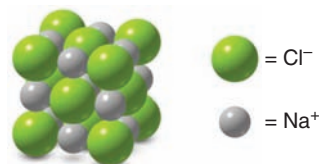


Atoms readily form ionic bonds when they can attain a noble gas configuration by gaining or losing just one or two electrons.

The type of bonding is determined by the location of an element in the periodic table. An ionic bond generally occurs when elements on the **far left** side of the periodic table combine with elements on the **far right** side, ignoring the noble gases, which form bonds only rarely. **The resulting ions are held together by extremely strong electrostatic interactions.** A positively charged cation formed from the element on the left side attracts a negatively charged anion formed from the element on the right side. The resulting **salts** are seen in many of the inorganic compounds with which you are familiar. Sodium chloride (NaCl) is common table salt, and potassium iodide (KI) is an essential nutrient added to make iodized salt.

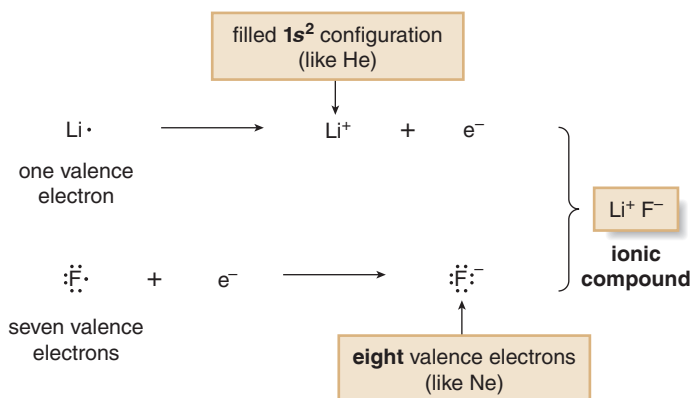
Ionic compounds form extended crystal lattices that maximize the positive and negative electrostatic interactions. In NaCl, each positively charged Na^+ ion is surrounded by six negatively charged Cl^- ions, and each Cl^- ion is surrounded by six Na^+ ions.

NaCl—An ionic crystalline lattice



Lithium fluoride, LiF, is an example of an ionic compound.

- The element **lithium**, located in group 1A of the periodic table, has just one valence electron in its second shell. If this electron is lost, lithium forms the cation Li^+ having no electrons in the second shell. However, it will have a stable electronic arrangement with two electrons in the first shell like helium.
- The element **fluorine**, located in group 7A of the periodic table, has seven valence electrons. By gaining one it forms the anion F^- , which has a filled valence shell (an octet of electrons), like neon.
- Thus, lithium fluoride is a stable ionic compound.



- The transfer of electrons forms stable salts composed of cations and anions.

A **compound** may have either ionic or covalent bonds. A **molecule** has only covalent bonds.

The second type of bonding, **covalent bonding**, occurs with elements like carbon in the middle of the periodic table, which would otherwise have to gain or lose several electrons to form an ion with a complete valence shell. A **covalent bond is a two-electron bond**, and a compound with covalent bonds is called a **molecule**. Covalent bonds also form between two elements from the same side of the table, such as two hydrogen atoms or two chlorine atoms. H_2 , Cl_2 , and CH_4 are all examples of covalent molecules.

Problem 1.3

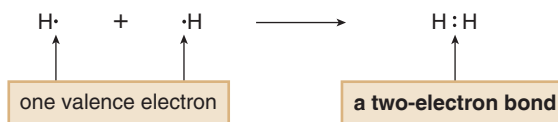
Label each bond in the following compounds as ionic or covalent.

- a. F_2 b. LiBr c. CH_3CH_3 d. NaNH_2

Problem 1.4

An element like fluorine forms either ionic or covalent bonds, depending on the identity of the element to which it bonds. What type of bonding is observed in each compound: (a) NaF , a toothpaste ingredient added to strengthen tooth enamel; (b) CFC_l_3 , a chlorofluorocarbon once widely used as an aerosol propellant? Explain why a difference is observed.

How many covalent bonds will a particular atom typically form? As you might expect, it depends on the location of the atom in the periodic table. In the first row, **hydrogen forms one covalent bond** using its one valence electron. When two hydrogen atoms are joined in a bond, each has a filled valence shell of two electrons.



Second-row elements can have no more than eight valence electrons around them. For neutral molecules, two consequences result.

- **Atoms with one, two, three, or four valence electrons form one, two, three, or four bonds**, respectively, in neutral molecules.
- **Atoms with five or more valence electrons** form enough bonds to give an octet. This results in the following simple equation:

**predicted
number of bonds** = 8 - **number of valence electrons**

For example, B has three valence electrons, so it forms three bonds, as in BF_3 . N has five valence electrons, so it also forms three bonds ($8 - 5 = 3$ bonds), as in NH_3 .

These guidelines are used in Figure 1.3 to summarize the usual number of bonds formed by the common atoms in organic compounds. Notice that when second-row elements form fewer than four bonds their octets consist of both **bonding (shared) electrons** and **nonbonding (unshared) electrons**. Unshared electrons are also called **lone pairs**.

Problem 1.5

How many covalent bonds are predicted for each atom?

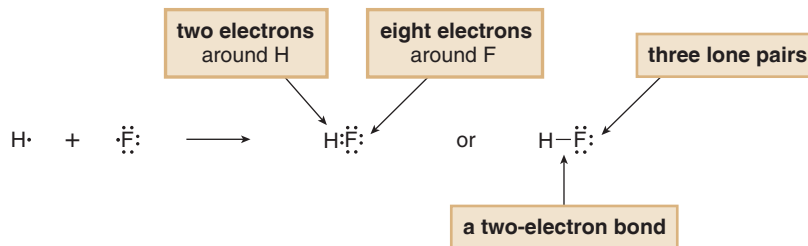
- a. O b. Al c. Br d. Si

1.3 Lewis Structures

Lewis structures are electron dot representations for molecules. There are three general rules for drawing Lewis structures.

1. Draw only the valence electrons.
2. Give every second-row element no more than eight electrons.
3. Give each hydrogen two electrons.

To draw a Lewis structure for a diatomic molecule like **HF**, recall that hydrogen has one valence electron and fluorine has seven. H and F each donate one electron to form a two-electron bond. The resulting molecule gives both H and F a filled valence shell.



In a Lewis structure, a *solid line* indicates a two-electron covalent bond.

Figure 1.3

Summary: The usual number of bonds of common neutral atoms

			<div style="border: 1px solid black; padding: 2px;">nonbonded electron pair</div>				
	—H	 —C— 	↓ · · —N— 	↓ · · —O— · ·	↓ · · —X: · ·	X = F, Cl, Br, I	
number of bonds →	1	4	3	2	1		
number of nonbonded electron pairs →	0	0	1	2	3		

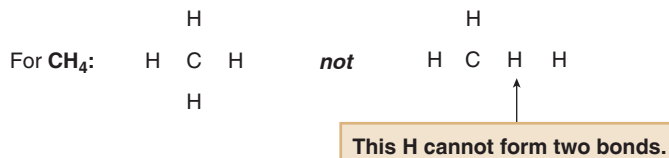
1.3A A Procedure for Drawing Lewis Structures

Drawing a Lewis structure for larger molecules is easier if you follow a stepwise procedure.

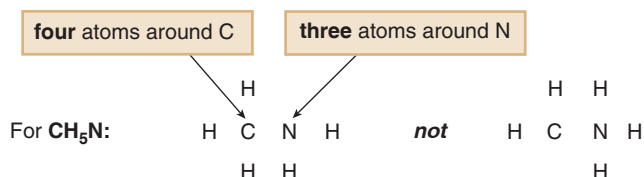
HOW TO Draw a Lewis Structure

Step [1] Arrange atoms next to each other that you think are bonded together.

- Always place hydrogen atoms and halogen atoms on the periphery because H and X (X = F, Cl, Br, and I) form only one bond each.



- As a first approximation, place no more atoms around an atom than the number of bonds it usually forms.



- In truth, the proper arrangement of atoms may not be obvious, or more than one arrangement may be possible (Section 1.4A). Even in many simple molecules, the connectivity between atoms must be determined experimentally.

Step [2] Count the electrons.

- Count the number of valence electrons from all atoms.
- Add one electron for each negative charge.
- Subtract one electron for each positive charge.
- This sum gives the total number of electrons that must be used in drawing the Lewis structure.

Step [3] Arrange the electrons around the atoms.

- Place a bond between every two atoms, giving two electrons to each H and no more than eight to any second-row atom.
- Use all remaining electrons to fill octets with lone pairs.
- If all valence electrons are used and an atom does not have an octet, form multiple bonds, as shown in Sample Problem 1.3.

Step [4] Assign formal charges to all atoms.

- Formal charges are discussed in Section 1.3C.

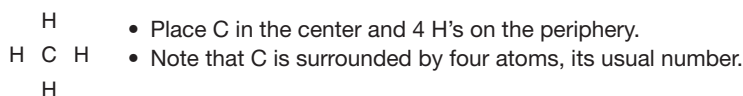
Sample Problems 1.1 and 1.2 illustrate how to draw Lewis structures in some simple organic molecules.

Sample Problem 1.1

Draw a Lewis structure for methane, CH_4 .

Solution

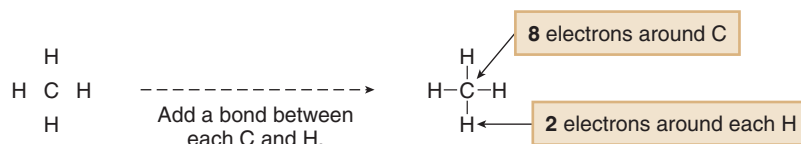
Step [1] Arrange the atoms.



Step [2] Count the electrons.

$$\begin{array}{rcl}
 1 \text{ C} \times 4 \text{ e}^- & = & 4 \text{ e}^- \\
 4 \text{ H} \times 1 \text{ e}^- & = & 4 \text{ e}^- \\
 \hline
 & & 8 \text{ e}^- \text{ total}
 \end{array}$$

Step [3] Add the bonds and lone pairs.



Adding four two-electron bonds around carbon uses all eight valence electrons, and so there are no lone pairs. To check whether a Lewis structure is valid, we must answer YES to three questions:

- Have all the electrons been used?
- Is each H surrounded by two electrons?
- Is each second-row element surrounded by no more than eight electrons?

The answer to all three questions is YES, so the Lewis structure drawn for CH_4 is valid.

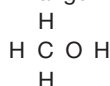
Sample Problem 1.2

Draw a Lewis structure for methanol, a compound with molecular formula CH_4O .

Solution

Step [1]

Arrange the atoms.



- four atoms around C
- two atoms around O

Step [2]

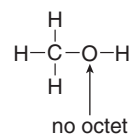
Count the electrons.

$$\begin{array}{rcl} 1 \text{ C} \times 4 \text{ e}^- & = & 4 \text{ e}^- \\ 1 \text{ O} \times 6 \text{ e}^- & = & 6 \text{ e}^- \\ 4 \text{ H} \times 1 \text{ e}^- & = & 4 \text{ e}^- \\ \hline & & 14 \text{ e}^- \text{ total} \end{array}$$

Step [3]

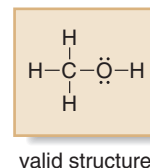
Add the bonds and lone pairs.

Add bonds first...



only 10 electrons used

...then lone pairs.



In Step [3], placing bonds between all atoms uses only 10 electrons, and the O atom does not yet have a complete octet. To complete the structure, give the O atom two nonbonded electron pairs. This uses all 14 electrons, giving every H two electrons and every second-row element eight. We have now drawn a valid Lewis structure.

Problem 1.6

Draw a valid Lewis structure for each species:

- a. CH_3CH_3 b. CH_5N c. CH_3^- d. CH_3Cl

1.3B Multiple Bonds

Sample Problem 1.3 illustrates two examples when multiple bonds are needed in Lewis structures.

Sample Problem 1.3

Draw a Lewis structure for each compound. Assume the atoms are arranged as follows:

- a. ethylene, C_2H_4 b. acetylene, C_2H_2
- $$\begin{array}{ccc} \text{H} & \text{C} & \text{C} & \text{H} \\ & & & \\ & \text{H} & & \text{H} \end{array}$$

Solution

- a. **Ethylene, C_2H_4 :** Follow Steps [1] to [3] to draw a Lewis structure. After placing five bonds between the atoms and adding the two remaining electrons as a lone pair, one C still has no octet.

Step [2]

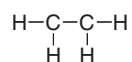
Count the electrons.

$$\begin{array}{rcl} 2 \text{ C} \times 4 \text{ e}^- & = & 8 \text{ e}^- \\ 4 \text{ H} \times 1 \text{ e}^- & = & 4 \text{ e}^- \\ \hline & & 12 \text{ e}^- \text{ total} \end{array}$$

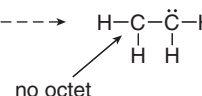
Step [3]

Add the bonds and lone pairs.

Add bonds first...



...then lone pairs.



The number of electrons “owned” by an atom is determined by its number of bonds and lone pairs.

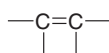
- An atom “owns” *all* of its unshared electrons and *half* of its shared electrons.

$$\boxed{\text{number of electrons owned}} = \boxed{\text{number of unshared electrons}} + \frac{1}{2} \left[\boxed{\text{number of shared electrons}} \right]$$

The number of electrons “owned” by different carbon atoms is indicated in the following examples:



- C shares eight electrons.
- C “owns” **four** electrons.



- Each C shares eight electrons.
- Each C “owns” **four** electrons.

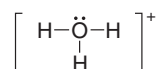


- C shares six electrons.
- C has two unshared electrons.
- C “owns” **five** electrons.

Sample Problem 1.4 illustrates how formal charge is calculated on the atoms of a polyatomic ion. **The sum of the formal charges on the individual atoms equals the net charge on the molecule or ion.**

Sample Problem 1.4

Determine the formal charge on each atom in the ion H_3O^+ .



Solution

For each atom, two steps are needed:

Step [1] Determine the number of electrons an atom “owns.”

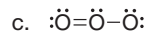
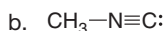
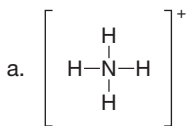
Step [2] Subtract this sum from its number of valence electrons.

O atom	H atoms
[1] number of electrons “owned” by O $2 + \frac{1}{2}(6) = 5$	[1] number of electrons “owned” by each H $0 + \frac{1}{2}(2) = 1$
[2] formal charge on O $6 - 5 = \boxed{+1}$	[2] formal charge on each H $1 - 1 = \boxed{0}$

The formal charge on each H is 0. The formal charge on oxygen is +1. The overall charge on the ion is the sum of all of the formal charges; $0 + 0 + 0 + 1 = +1$.

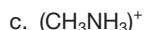
Problem 1.8

Calculate the formal charge on each second-row atom:



Problem 1.9

Draw a Lewis structure for each ion:



Sometimes it is easier to count bonds, rather than shared electrons when determining formal charge.

$$\frac{1}{2}[\text{number of shared electrons}] = \text{number of bonds}$$

When you first add formal charges to Lewis structures, use the procedure in Sample Problem 1.4. With practice, you will notice that certain bonding patterns always result in the same formal charge. For example, any N atom with four bonds (and, thus no lone pairs) has a +1 formal charge. Table 1.1 lists the bonding patterns and resulting formal charges for carbon, nitrogen, and oxygen.

A shortcut method to determine the number of bonds in a Lewis structure is given in the *Student Study Guide/Solutions Manual* (page 1–4).

Table 1.1 Formal Charge Observed with Common Bonding Patterns for C, N, and O

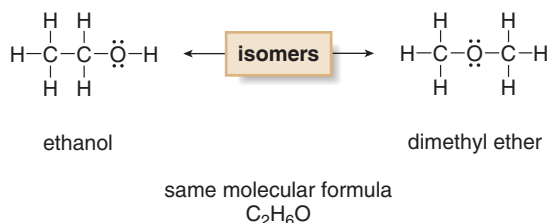
Atom	Number of valence electrons	Formal charge		
		+1	0	-1
C	4	$\begin{array}{c} + \\ \\ \text{---C---} \\ \end{array}$	$\begin{array}{c} \\ \text{---C---} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \\ \text{---}\ddot{\text{C}}\text{---} \\ \end{array}$
N	5	$\begin{array}{c} + \\ \\ \text{---N---} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \\ \text{---}\ddot{\text{N}}\text{---} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \\ \text{---}\ddot{\text{N}}\text{---} \\ \end{array}$
O	6	$\begin{array}{c} + \\ \\ \text{---}\ddot{\text{O}}\text{---} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \\ \text{---}\ddot{\text{O}}\text{---} \\ \end{array}$	$\begin{array}{c} \cdot\cdot \\ \\ \text{---}\ddot{\text{O}}\text{---} \\ \end{array}$

1.4 Lewis Structures Continued

The discussion of Lewis structures concludes with the introduction of isomers and exceptions to the octet rule.

1.4A Isomers

In drawing a Lewis structure for a molecule with several atoms, sometimes more than one arrangement of atoms is possible for a given molecular formula. For example, there are two acceptable arrangements of atoms for the molecular formula $\text{C}_2\text{H}_6\text{O}$.



Both are valid Lewis structures, and both molecules exist. One is called ethanol, and the other, dimethyl ether. These two compounds are called **isomers**.

- **Isomers** are different molecules having the same molecular formula.

Ethanol and dimethyl ether are **constitutional isomers** because they have the same molecular formula, but the **connectivity of their atoms is different**. For example, ethanol has one C–C bond and one O–H bond, whereas dimethyl ether has two C–O bonds. A second class of isomers, called **stereoisomers**, is introduced in Section 4.13B.

Problem 1.10

Draw Lewis structures for each molecular formula.

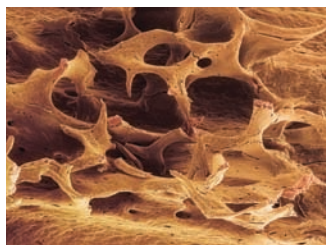
- a. $\text{C}_2\text{H}_4\text{Cl}_2$ (two isomers) b. $\text{C}_3\text{H}_8\text{O}$ (three isomers) c. C_3H_6 (two isomers)

1.4B Exceptions to the Octet Rule

Most of the common elements in organic compounds—**C, N, O, and the halogens**—follow the octet rule. Hydrogen is a notable exception, because it accommodates only two electrons in bonding. Additional exceptions include boron and beryllium (second-row elements in groups 3A and 2A, respectively), and elements in the third row (particularly phosphorus and sulfur).

Elements in Groups 2A and 3A

Elements in groups 2A and 3A of the periodic table, such as beryllium and boron, do not have enough valence electrons to form an octet in a neutral molecule. Lewis structures for BeH_2 and BF_3 show that these atoms have only four and six electrons, respectively, around the central atom. There is nothing we can do about this! There simply aren't enough electrons to form an octet.



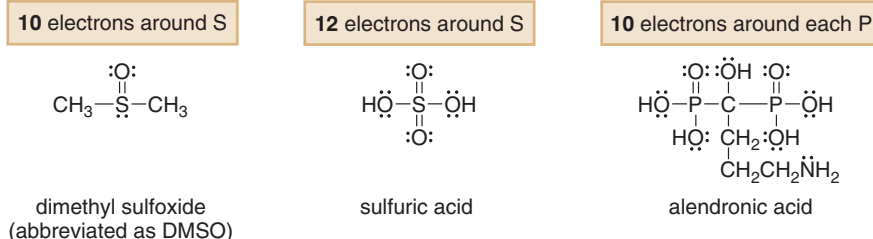
Alendronic acid, sold as a sodium salt under the trade name of **Fosamax**, is used to prevent osteoporosis in women. Osteoporosis decreases bone density, as shown by comparing normal bone (top) with brittle bone (bottom).



Because the Be and B atoms each have less than an octet of electrons, these molecules are highly reactive.

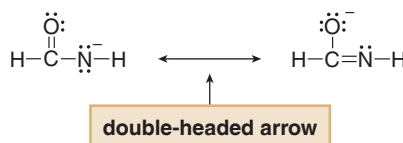
Elements in the Third Row

A second exception to the octet rule occurs with some elements located in the third row and later in the periodic table. These elements have empty *d* orbitals available to accept electrons, and thus they may have **more than eight electrons** around them. For organic chemists, the two most common elements in this category are phosphorus and sulfur, which can have 10 or even 12 electrons around them. Examples of these phosphorus and sulfur compounds include the following:



1.5 Resonance

Some molecules can't be adequately represented by a single Lewis structure. For example, two valid Lewis structures can be drawn for the anion $(\text{HCONH})^-$. One structure has a negatively charged N atom and a C–O double bond; the other has a negatively charged O atom and a C–N double bond. These structures are called **resonance structures** or **resonance forms**. A **double-headed arrow** is used to separate two resonance structures.



- **Resonance structures** are two Lewis structures having the *same* placement of atoms but a *different* arrangement of electrons.

Which resonance structure is an accurate representation for $(\text{HCONH})^-$? **The answer is neither of them.** The true structure is a composite of both resonance forms, and is called a **resonance hybrid**. The hybrid shows characteristics of **both** resonance structures.

Each resonance structure implies that electron pairs are localized in bonds or on atoms. In actuality, resonance allows certain electron pairs to be **delocalized** over two or more atoms, and this delocalization of electron density adds stability. **A molecule with two or more resonance structures is said to be resonance stabilized.** We will return to the resonance hybrid in Section 1.5C. First, however, we examine the general principles of resonance theory and learn how to interconvert two or more resonance structures.

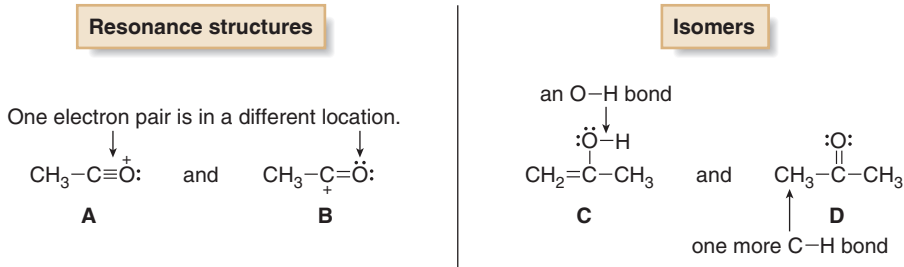
1.5A An Introduction to Resonance Theory

Keep in mind the following basic principles of resonance theory.

- Resonance structures are not real. An individual resonance structure does not accurately represent the structure of a molecule or ion. Only the hybrid does.
- Resonance structures are *not* in equilibrium with each other. There is no movement of electrons from one form to another.
- Resonance structures are *not* isomers. Two isomers differ in the arrangement of *both* atoms and electrons, whereas resonance structures differ *only* in the *arrangement of electrons*.

Resonance structures are different ways of drawing the same compound. Two resonance structures are *not* different compounds.

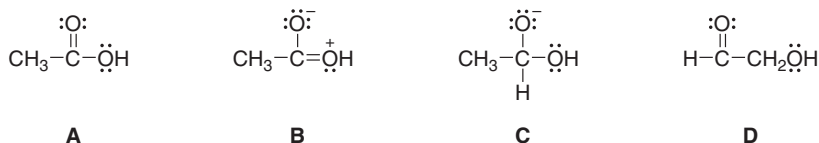
For example, ions **A** and **B** are resonance structures because the atom position is the same in both compounds, but the location of an electron pair is different. In contrast, compounds **C** and **D** are isomers since the atom placement is different; **C** has an O–H bond, and **D** has an additional C–H bond.



Problem 1.11 Classify each pair of compounds as isomers or resonance structures.



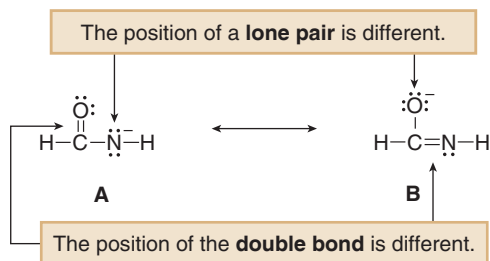
Problem 1.12 Considering structures **A–D**, classify each pair of compounds as isomers, resonance structures, or neither: (a) **A** and **B**; (b) **A** and **C**; (c) **A** and **D**; (d) **B** and **D**.



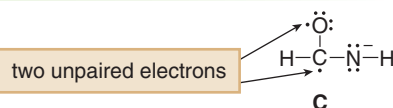
1.5B Drawing Resonance Structures

To draw resonance structures, use the three rules that follow:

Rule [1] Two resonance structures differ in the position of multiple bonds and nonbonded electrons. The placement of atoms and single bonds always stays the same.

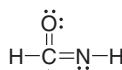


Rule [2] Two resonance structures must have the same number of unpaired electrons.



- **A** and **B** have no unpaired electrons.
- **C** is *not* a resonance structure of **A** and **B**.

Rule [3] Resonance structures must be valid Lewis structures. Hydrogen must have two electrons and no second-row element can have more than eight electrons.



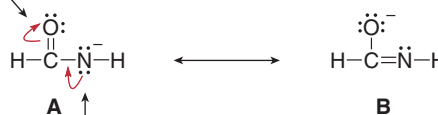
10 electrons around C
not a valid Lewis structure

Curved arrow notation is a convention that shows how electron position differs between the two resonance forms.

- *Curved arrow notation shows the movement of an electron pair.* The tail of the arrow always begins at an electron pair, either in a bond or lone pair. The head points to where the electron pair “moves.”

A curved arrow always begins at an electron pair. It ends at an atom or a bond.

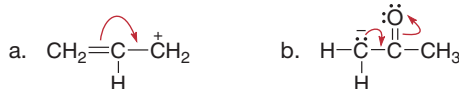
Move an electron pair to O.



Use this electron pair to form a double bond.

Resonance structures **A** and **B** differ in the location of two electron pairs, so two curved arrows are needed. To convert **A** to **B**, take the lone pair on N and form a double bond between C and N. Then, move an electron pair in the C–O double bond to form a lone pair on O. Curved arrows thus show how to reposition the electrons in converting one resonance form to another. **The electrons themselves do not actually move.** Sample Problem 1.5 illustrates the use of curved arrows to convert one resonance structure to another.

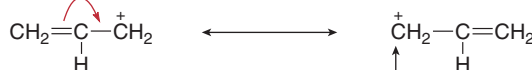
Sample Problem 1.5 Follow the curved arrows to draw a second resonance structure for each ion.



Solution

- a. The curved arrow tells us to move **one** electron pair in the double bond to the adjacent C–C bond. Then determine the formal charge on any atom whose bonding is different.

Move one electron pair...



...then assign the formal charge (+1).

Positively charged carbon atoms are called **carbocations**. Carbocations are unstable intermediates because they contain a carbon atom that is lacking an octet of electrons.

- b. **Two** curved arrows tell us to move **two** electron pairs. The second resonance structure has a formal charge of (-1) on O.

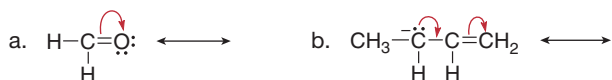
Move two electron pairs...



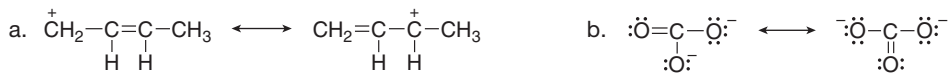
...then calculate formal charges.

This type of resonance-stabilized anion is called an **enolate anion**. Enolates are important intermediates in many organic reactions, and all of Chapters 23 and 24 is devoted to their preparation and reactions.

Problem 1.13 Follow the curved arrows to draw a second resonance structure for each species.



Problem 1.14 Use curved arrow notation to show how the first resonance structure can be converted to the second.

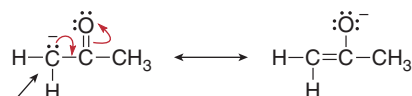


Two resonance structures can have exactly the same kinds of bonds, as they do in the carbocation in Sample Problem 1.5a, or they may have different types of bonds, as they do in the enolate in Sample Problem 1.5b. Either possibility is fine as long as the individual resonance structures are valid Lewis structures.

The ability to draw and manipulate resonance structures is an important skill that will be needed throughout your study of organic chemistry. With practice, you will begin to recognize certain common bonding patterns for which more than one Lewis structure can be drawn. For now, notice that two different resonance structures can be drawn in the following situations:

- When a lone pair is located on an atom directly bonded to a multiple bond.

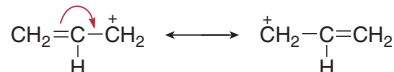
lone pair adjacent to C=C



lone pair adjacent to C=O

- When an atom bearing a (+) charge is bonded to either a multiple bond or an atom with a lone pair.

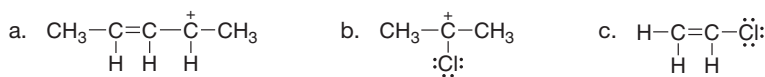
(+) charge adjacent to a double bond



(+) charge adjacent to an atom with a lone pair



Draw a second resonance structure for each species.



1.5C The Resonance Hybrid

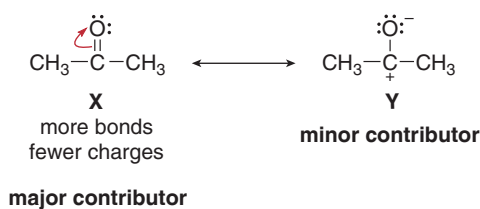
The **resonance hybrid** is the composite of all possible resonance structures. In the resonance hybrid, the electron pairs drawn in different locations in individual resonance structures are *delocalized*.

- The resonance hybrid is more stable than any resonance structure because it delocalizes electron density over a larger volume.

What does the hybrid look like? When all resonance forms are identical, as they were in the carbocation in Sample Problem 1.5a, each resonance form contributes **equally** to the hybrid.

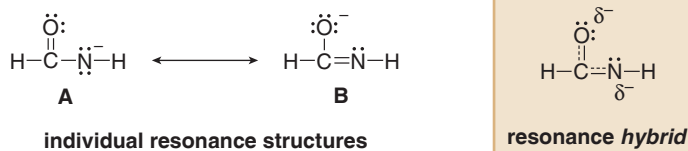
When two resonance structures are different, the hybrid looks more like the “better” resonance structure. The “better” resonance structure is called the **major contributor** to the hybrid, and all others are **minor contributors**. The hybrid is the weighted average of the contributing resonance structures. What makes one resonance structure “better” than another? There are many factors, but for now, we will learn just two.

- A “better” resonance structure is one that has *more bonds* and *fewer charges*.



Comparing resonance structures **X** and **Y**, **X** is the major contributor because it has more bonds and fewer charges. Thus, the hybrid looks more like **X** than **Y**.

How can we draw a hybrid, which has delocalized electron density? First, we must determine what is different in the resonance structures. Two differences commonly seen are the **position of a multiple bond** and the **site of a charge**. The anion $(\text{HCONH})^-$ illustrates two conventions for drawing resonance hybrids.

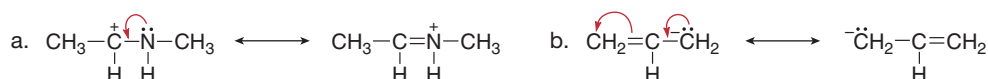


Common symbols and conventions used in organic chemistry are listed on the inside back cover.

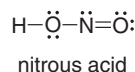
- **Double bond position.** Structure **A** has a C–O double bond, whereas structure **B** has a C–N double bond. A dashed line in the hybrid indicates partial double bond character between these atoms.
- **Location of the charge.** A negative charge resides on different atoms in **A** and **B**. The symbol δ^- (for a partial negative charge) indicates that the charge is delocalized on the N and O atoms in the hybrid.

This discussion of resonance is meant to serve as an introduction only. You will learn many more facets of resonance theory in later chapters. In Chapter 2, for example, the enormous effect of resonance on acidity is discussed.

Problem 1.16 Label the resonance structures in each pair as major, minor, or equal contributors to the hybrid. Then draw the hybrid.



Problem 1.17 Draw a second resonance structure for nitrous acid. Label each resonance structure as a major, minor, or equal contributor to the hybrid. Then draw the resonance hybrid.



1.6 Determining Molecular Shape

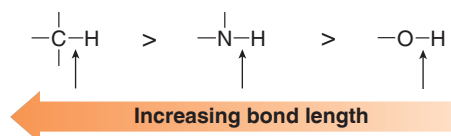
We can now use Lewis structures to determine the shape around a particular atom in a molecule. Consider the H_2O molecule. The Lewis structure tells us only which atoms are connected to each other, but it implies nothing about the geometry. What does the overall molecule look like? Is H_2O a bent or linear molecule? Two variables define a molecule's structure: **bond length** and **bond angle**.

1.6A Bond Length

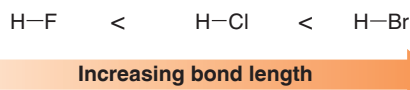
Although the SI unit for bond length is the picometer (pm), the angstrom (\AA) is still widely used in the chemical literature; $1 \text{ \AA} = 10^{-10} \text{ m}$. As a result, $1 \text{ pm} = 10^{-2} \text{ \AA}$, and $95.8 \text{ pm} = 0.958 \text{ \AA}$.

Bond length is the average distance between the centers of two bonded nuclei. Bond lengths are typically reported in picometers (pm), where $1 \text{ pm} = 10^{-12} \text{ m}$. For example, the O–H bond length in H_2O is 95.8 pm. Average bond lengths for common bonds are listed in Table 1.2.

- Bond length *decreases* across a row of the periodic table as the size of the atom *decreases*.



- Bond length *increases* down a column of the periodic table as the size of an atom *increases*.



Learn these general trends. Often knowing such trends is more useful than learning a set of exact numbers, because we are usually interested in comparisons rather than absolute values.

Table 1.2 Average Bond Lengths

Bond	Length (pm)	Bond	Length (pm)	Bond	Length (pm)
H–H	74	H–F	92	C–F	133
C–H	109	H–Cl	127	C–Cl	177
N–H	101	H–Br	141	C–Br	194
O–H	96	H–I	161	C–I	213

1.6B Bond Angle

Bond angle determines the shape around any atom bonded to two other atoms. To determine the bond angle and shape around a given atom, we must first determine how many groups surround the atom. **A group is either an atom or a lone pair of electrons.** Then we use the **valence shell electron pair repulsion (VSEPR) theory** to determine the shape. VSEPR is based on the fact that electron pairs repel each other; thus:

- The most stable arrangement keeps these groups as far away from each other as possible.

A second-row element has only three possible arrangements, defined by the number of groups surrounding it.

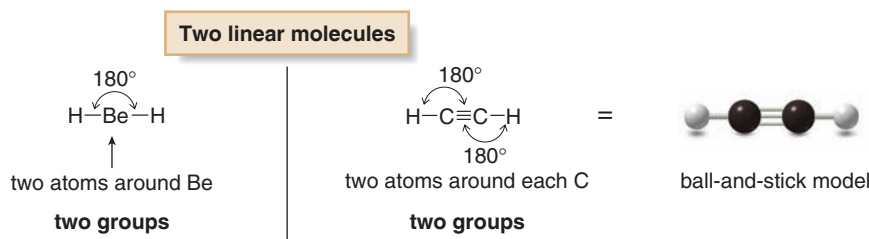
To determine geometry:
[1] Draw a valid Lewis structure; [2] count groups around a given atom.

Number of groups	Geometry	Bond angle
• two groups	linear	180°
• three groups	trigonal planar	120°
• four groups	tetrahedral	109.5°

Let's examine several molecules to illustrate this phenomenon. In each example, we first need a valid Lewis structure, and then we merely count groups around a given atom to predict its geometry.

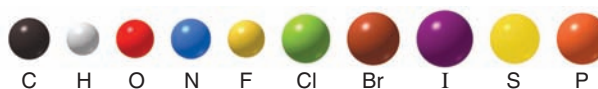
Two Groups Around an Atom

Any atom surrounded by only two groups is linear and has a bond angle of 180°. Two examples illustrating this geometry are **BeH₂** (beryllium hydride) and **HC≡CH** (acetylene). We consider each carbon atom in acetylene *separately*. Because each C is surrounded by two atoms and no lone pairs, each H–C–C bond angle in acetylene is 180°, and therefore all four atoms are linear.



Acetylene illustrates another important feature: **ignore multiple bonds in predicting geometry. Count only atoms and lone pairs.**

We will begin to represent molecules with models having balls for atoms and sticks for bonds, as in the ball-and-stick model of acetylene just shown. These representations are analogous to a set of molecular models. Balls are color-coded using accepted conventions: carbon (black), hydrogen (white or gray), oxygen (red), and so forth, as shown.

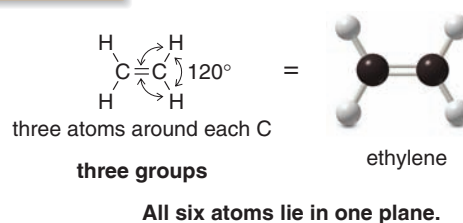
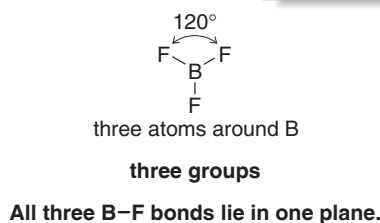


Three Groups Around an Atom

Any atom surrounded by three groups is trigonal planar and has bond angles of 120°. Two examples illustrating this geometry are **BF₃** (boron trifluoride) and **CH₂=CH₂** (ethylene). *Each* carbon atom of ethylene is surrounded by three atoms and no lone pairs, making *each* H–C–C bond angle 120°.

Most students in organic chemistry find that building models helps them visualize the shape of molecules. Invest in a set of models *now*.

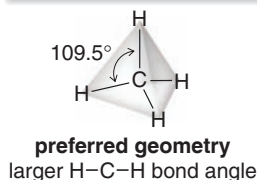
Two trigonal planar molecules



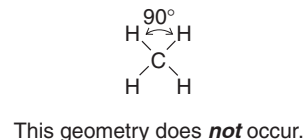
Four Groups Around an Atom

Any atom surrounded by four groups is **tetrahedral** and has bond angles of approximately **109.5°**. For example, the simple organic compound methane, CH_4 , has a central carbon atom with bonds to four hydrogen atoms, each pointing to a corner of a tetrahedron. This arrangement keeps four groups farther apart than a square planar arrangement in which all bond angles would be only 90°.

Tetrahedral arrangement

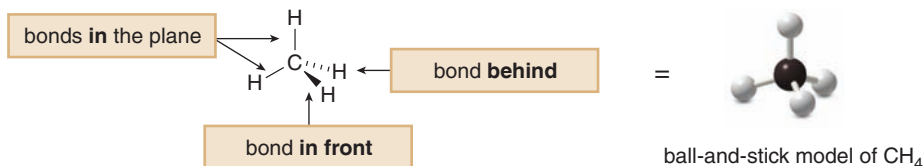


Square planar arrangement

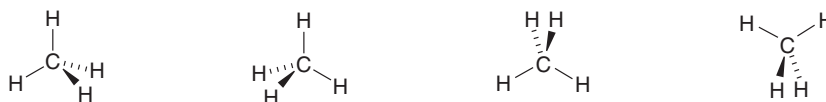


How can we represent the three-dimensional geometry of a tetrahedron on a two-dimensional piece of paper? **Place two of the bonds in the plane of the paper, one bond in front and one bond behind**, using the following conventions:

- A **solid line** is used for a bond *in* the plane.
- A **wedge** is used for a bond *in front* of the plane.
- A **dashed line** is used for a bond *behind* the plane.

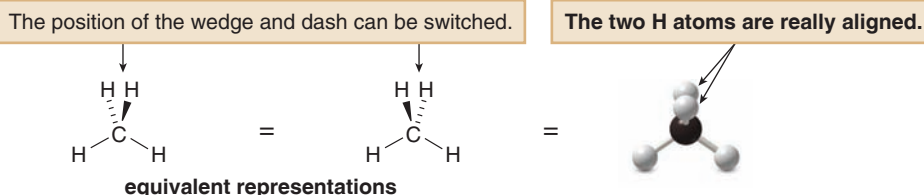


This is just one way to draw a tetrahedron for CH_4 . We can turn the molecule in many different ways, generating many equivalent representations. For example, all of the following are acceptable drawings for CH_4 .



Each drawing has two solid lines, one wedge, and one dashed line.

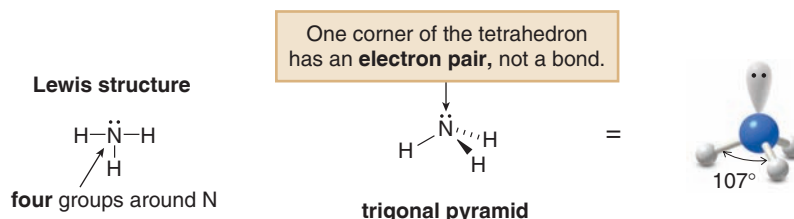
Finally, **wedges and dashes are used for groups that are really aligned one behind another**. It does not matter in the following two drawings whether the wedge or dash is skewed to the left or right, because the two H atoms are really aligned as shown in the three-dimensional model.



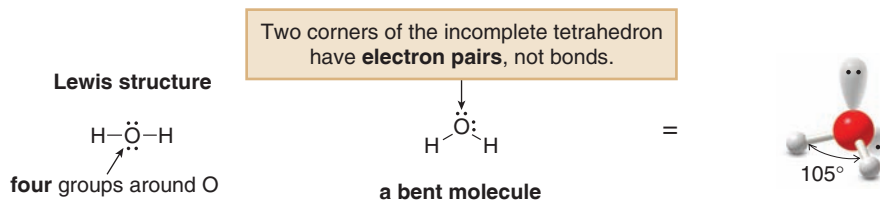
All carbons in stable molecules are **tetravalent**, but the geometry varies with the number of groups around the particular carbon.

Problem 1.18 Draw two different three-dimensional representations for CH_2Cl_2 (dichloromethane) using wedges and dashes.

Ammonia (NH_3) and water (H_2O) both have atoms surrounded by four groups, some of which are lone pairs. In NH_3 , the three H atoms and one lone pair around N point to the corners of a tetrahedron. The H–N–H bond angle of 107° is close to the theoretical tetrahedral bond angle of 109.5° . This molecular shape is referred to as a **trigonal pyramid**, because one of the groups around the N is a nonbonded electron pair, not another atom.



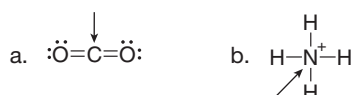
In H_2O , the two H atoms and two lone pairs around O point to the corners of a tetrahedron. The H–O–H bond angle of 105° is close to the theoretical tetrahedral bond angle of 109.5° . Water has a **bent** molecular shape, because two of the groups around oxygen are lone pairs of electrons.



In both NH_3 and H_2O the bond angle is somewhat smaller than the theoretical tetrahedral bond angle because of repulsion of the lone pairs of electrons. The bonded atoms are compressed into a smaller space with a smaller bond angle.

Predicting geometry based on counting groups is summarized in Figure 1.4.

Sample Problem 1.6 Determine the geometry around the indicated atom in each species.



Solution

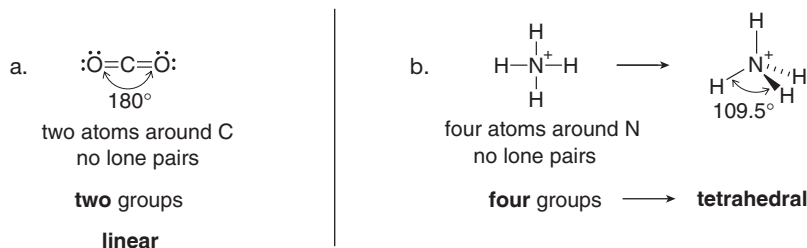
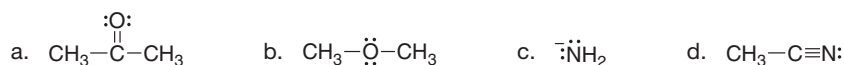


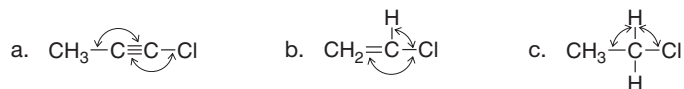
Figure 1.4
Summary: Determining geometry based on the number of groups

Number of groups around an atom	Geometry	Bond angle	Examples
2	linear	180°	BeH_2 , $\text{HC}\equiv\text{CH}$
3	trigonal planar	120°	BF_3 , $\text{CH}_2=\text{CH}_2$
4	tetrahedral	109.5°	CH_4 , NH_3 , H_2O

Problem 1.19 Determine the geometry around all second-row elements in each compound.

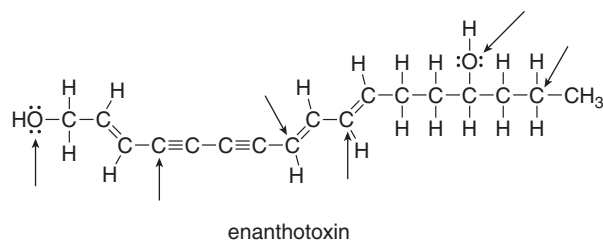


Problem 1.20 Predict the indicated bond angles in each compound.



Problem 1.21

Using the principles of VSEPR theory, you can predict the geometry around any atom in any molecule, no matter how complex. Enanthotoxin is a poisonous compound isolated from a common variety of hemlock grown in England. Predict the geometry around the indicated atoms in enanthotoxin.



1.7 Drawing Organic Structures

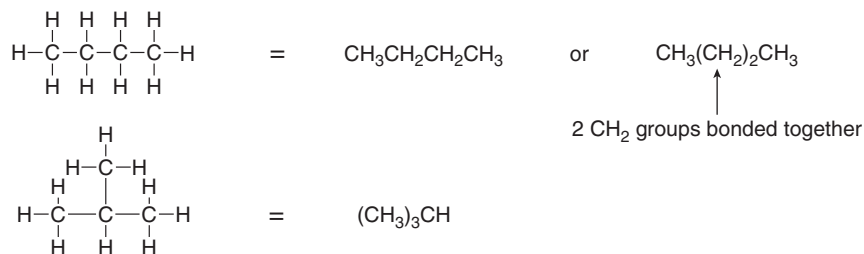
Drawing organic molecules presents a special challenge. Because they often contain many atoms, we need shorthand methods to simplify their structures. The two main types of shorthand representations used for organic compounds are **condensed structures** and **skeletal structures**.

1.7A Condensed Structures

Condensed structures are most often used for compounds having a chain of atoms bonded together, rather than a ring. The following conventions are used:

- All of the atoms are drawn in, but the two-electron bond lines are generally omitted.
- Atoms are usually drawn next to the atoms to which they are bonded.
- Parentheses are used around similar groups bonded to the same atom.
- Lone pairs are omitted.

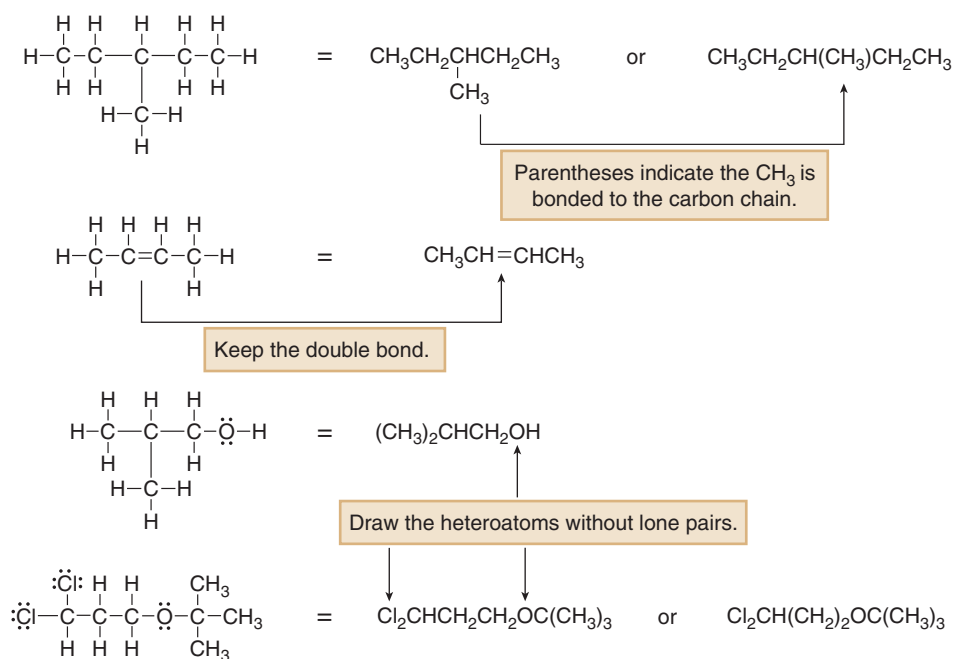
To interpret a condensed formula, it is usually best to start at the **left side** of the molecule and remember that the **carbon atoms must be tetravalent**. A carbon bonded to three H atoms becomes CH_3 ; a carbon bonded to two H atoms becomes CH_2 , and so forth. Two examples of condensed formulas for compounds having only carbon and hydrogen are given below.



Recall from the prologue:
A **heteroatom** is any atom that is not C or H.

Other examples of condensed structures with heteroatoms and carbon-carbon multiple bonds are given in Figure 1.5. You must learn how to convert a Lewis structure to a condensed structure, and vice versa.

Figure 1.5
Examples of condensed structures



Translating some condensed formulas is not obvious, and it will come only with practice. This is especially true for compounds containing a carbon–oxygen double bond. Some noteworthy examples in this category are given in Figure 1.6. While carbon–carbon double bonds are generally drawn in condensed structures, carbon–oxygen double bonds are usually omitted.

Sample Problem 1.7

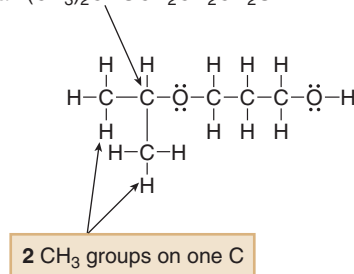
Convert each condensed formula to a Lewis structure.

- a. $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{OH}$ b. $\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{C}(\text{CH}_3)_3$

Solution

Start at the left and proceed to the right, making sure that each carbon has four bonds. Give any heteroatom enough lone pairs to have an octet.

- a. $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$



- b. $\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{C}(\text{CH}_3)_3$

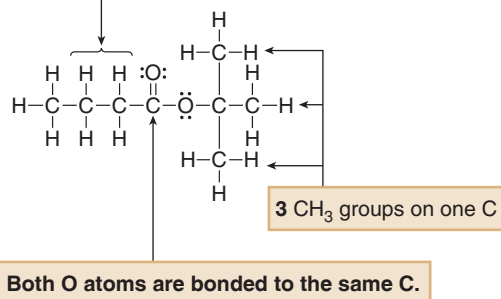
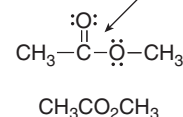
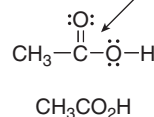
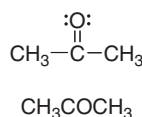
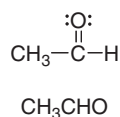


Figure 1.6
Condensed structures containing a C–O double bond



Both O atoms are bonded to the same C.

- Take special note of condensed structures with oxygen atoms. In these examples, the only way for all atoms to have an octet is by having a carbon–oxygen double bond.

Problem 1.22 Convert each condensed formula to a Lewis structure.

- a. $\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{CH}_3)_2$ c. $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CH}_2\text{CH}_3$
 b. $(\text{CH}_3)_2\text{CHCH}(\text{CH}_2\text{CH}_3)_2$ d. $(\text{CH}_3)_2\text{CHCHO}$

Problem 1.23 Simplify each condensed structure by using parentheses around similar groups.

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ c. $\text{HOCH}_2-\overset{\text{CH}_2\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$
 b. $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{CH}_2\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2\text{CH}_3$

Problem 1.24 During periods of strenuous exercise, the buildup of lactic acid $[\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}]$ causes the aching feeling in sore muscles. Convert this condensed structure to a Lewis structure of lactic acid.

1.7B Skeletal Structures

Skeletal structures are used for organic compounds containing both rings and chains of atoms. Three important rules are used to draw them:

- Assume there is a carbon atom at the junction of any two lines or at the end of any line.
- Assume there are enough hydrogens around each carbon to make it tetravalent.
- Draw in all heteroatoms and the hydrogens directly bonded to them.

Carbon chains are drawn in a zigzag fashion, and rings are drawn as polygons, as shown for hexane and cyclohexane.

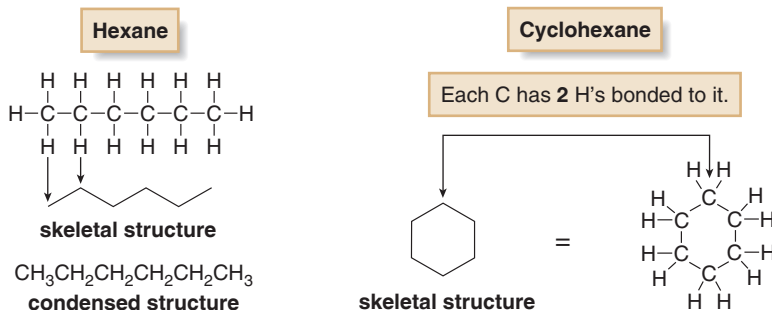
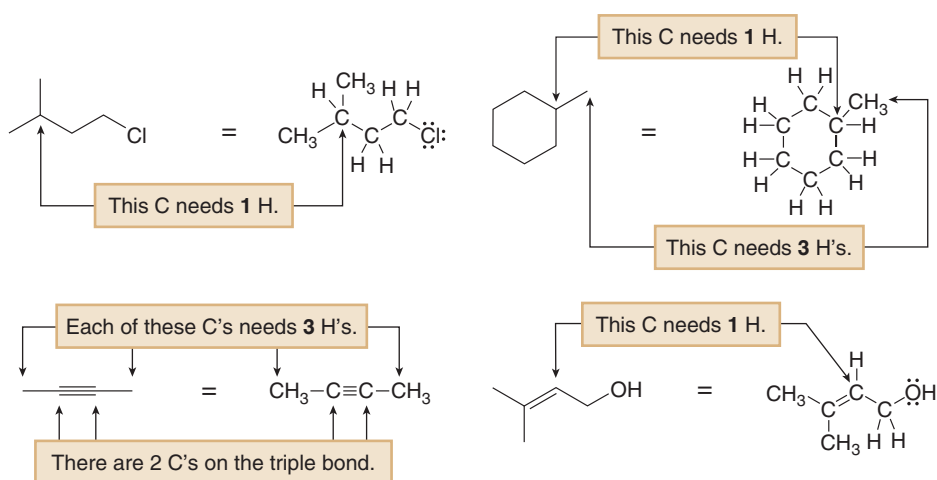


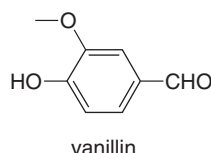
Figure 1.7 shows other examples of skeletal structures for a variety of Lewis structures, and Sample Problem 1.8 illustrates how to interpret the skeletal structure for a cyclic compound.

Figure 1.7
Examples of skeletal structures



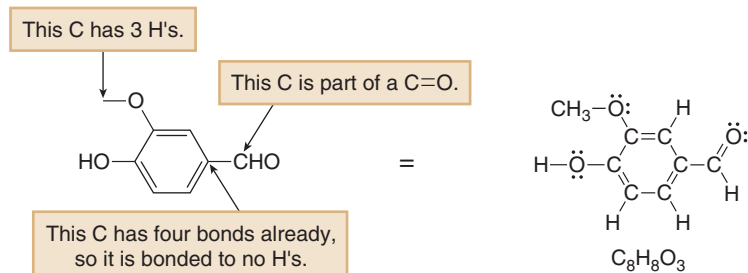
Sample Problem 1.8

Draw a complete structure for vanillin showing all H atoms and lone pairs. Vanillin is the principal component of the extract of the vanilla bean.



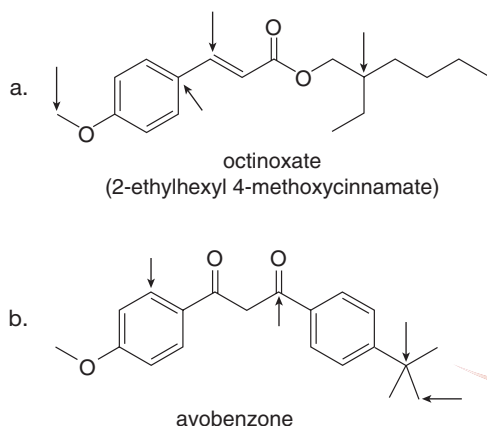
Solution

Skeletal structures have a C atom at the junction of any two lines and at the end of any line. Each C must have enough H's to make it tetravalent. In structures that contain a -CHO group, the C atom is doubly bonded to the O atom and singly bonded to H. Each O atom needs two lone pairs to have a complete octet.



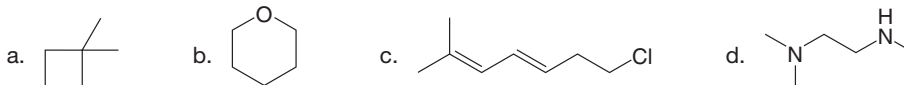
Problem 1.25

How many hydrogen atoms are present around each indicated carbon atom in the following molecules? Both compounds are active ingredients in some common sunscreens.

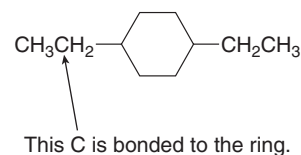
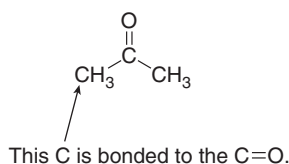
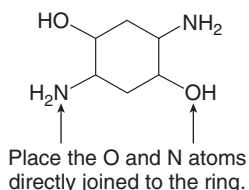


Problem 1.26

Convert each skeletal structure to a Lewis structure.



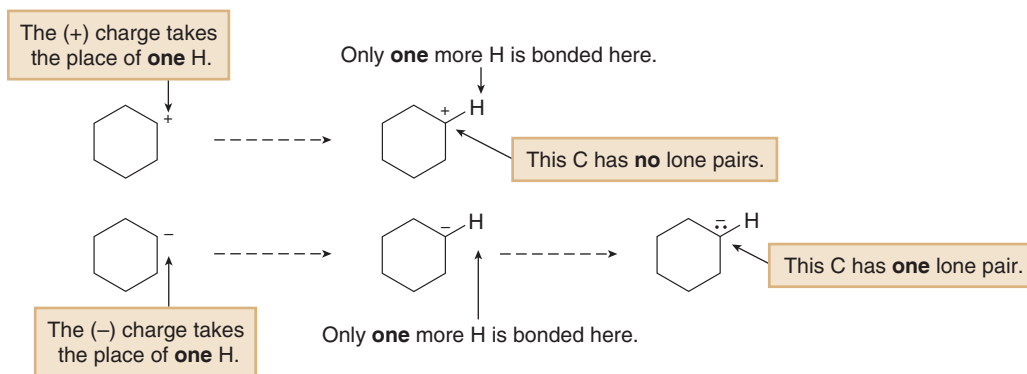
When heteroatoms are bonded to a carbon skeleton, the heteroatom is joined *directly* to the carbon to which it is bonded, with no H atoms in between. Thus, an OH group is drawn as OH or HO depending on where the OH is located. In contrast, when carbon appendages are bonded to a carbon skeleton, the H atoms will be drawn to the *right* of the carbon to which they are bonded regardless of the location.



1.7C Skeletal Structures with Charged Carbon Atoms

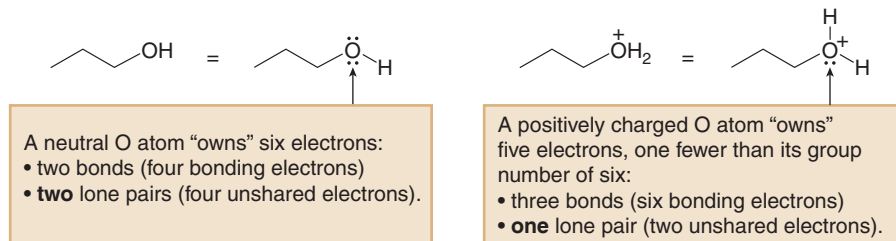
Take care in interpreting skeletal structures for positively and negatively charged carbon atoms, because *both* the hydrogen atoms *and* the lone pairs are omitted. Keep in mind the following:

- A charge on a carbon atom takes the place of **one** hydrogen atom.
- The charge determines the number of lone pairs. Negatively charged carbon atoms have one lone pair and positively charged carbon atoms have none.

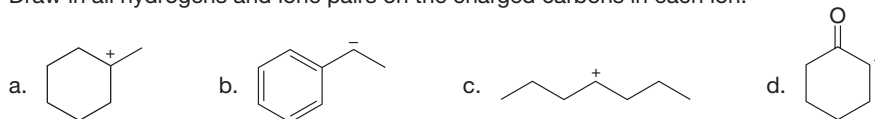


Skeletal structures often leave out lone pairs on heteroatoms, but *don't forget about them*.

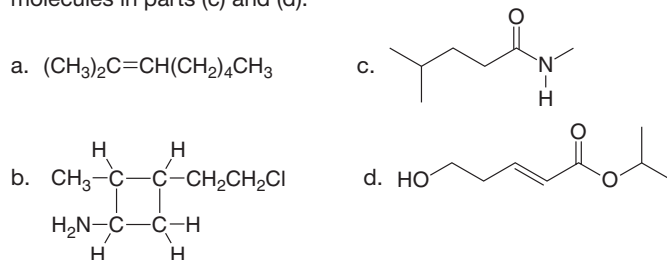
Use the formal charge on an atom to determine the number of lone pairs. For example, a neutral O atom with two bonds needs two additional lone pairs, and a positively charged O atom with three bonds needs only one lone pair.



Problem 1.27 Draw in all hydrogens and lone pairs on the charged carbons in each ion.



Problem 1.28 Draw a skeletal structure for the molecules in parts (a) and (b), and a condensed structure for the molecules in parts (c) and (d).

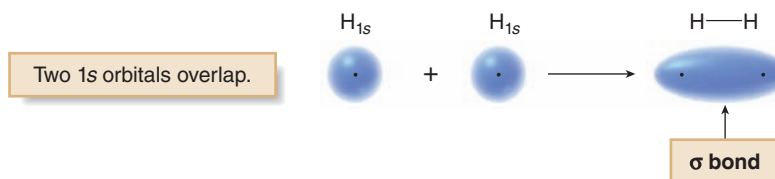


1.8 Hybridization

What orbitals do the first- and second-row atoms use to form bonds? Let's begin with hydrogen and then examine the orbitals used for bonding by atoms in the second row.

1.8A Hydrogen

Recall from Section 1.2 that two hydrogen atoms share each of their electrons to form H_2 . Thus, the $1s$ orbital on one H overlaps with the $1s$ orbital on the other H to form a bond that concentrates electron density between the two nuclei. This type of bond, called a σ (sigma) **bond**, is cylindrically symmetrical because the electrons forming the bond are distributed symmetrically about an imaginary line connecting the two nuclei.

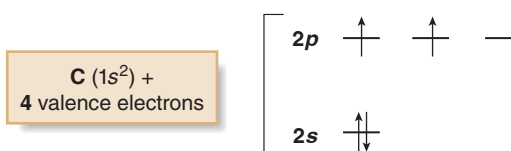


- A σ bond concentrates electron density on the axis that joins two nuclei. All single bonds are σ bonds.

1.8B Bonding in Methane

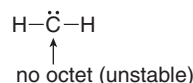
To account for the bonding patterns observed in more complex molecules, we must take a closer look at the $2s$ and $2p$ orbitals of atoms of the second row. Let's illustrate this with methane, CH_4 .

Carbon has two core electrons, plus **four valence electrons**. To fill atomic orbitals in the most stable arrangement, electrons are placed in the orbitals of lowest energy. For carbon, this places two in the $2s$ orbital and one each in two $2p$ orbitals.

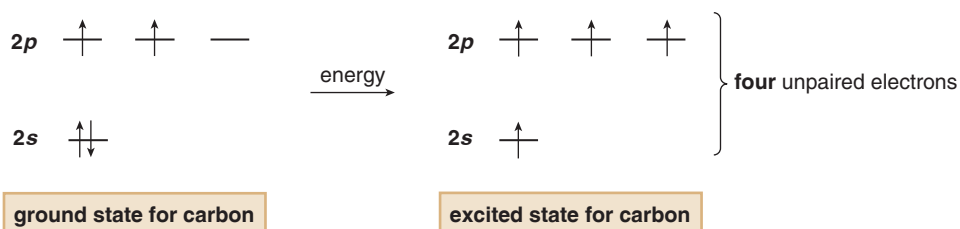


- This lowest energy arrangement of electrons for an atom is called its **ground state**.

In this description, **carbon should form only two bonds** because it has only two unpaired valence electrons, and CH_2 should be a stable molecule. In reality, however, CH_2 is a highly reactive species that cannot be isolated under typical laboratory conditions. In CH_2 , carbon would not have an octet of electrons.



There is a second possibility. Promotion of an electron from a $2s$ to a vacant $2p$ orbital would form **four** unpaired electrons for bonding. This process requires energy because it moves an electron to a higher energy orbital. This higher energy electron configuration is called an electronically **excited state**.



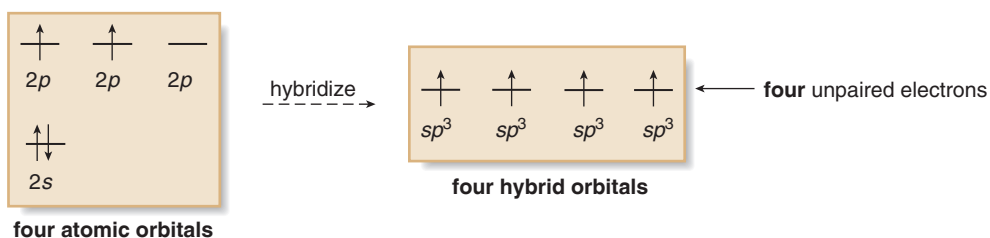
This description is still not adequate. Carbon would form two different types of bonds: three with $2p$ orbitals and one with a $2s$ orbital. **But experimental evidence points to carbon forming four identical bonds in methane.**

To solve this dilemma, chemists have proposed that atoms like carbon do not use pure s and pure p orbitals in forming bonds. Instead, atoms use a set of new orbitals called **hybrid orbitals**. The mathematical process by which these orbitals are formed is called **hybridization**.

- **Hybridization** is the combination of two or more atomic orbitals to form the same number of hybrid orbitals, each having the same shape and energy.

Hybridization of one $2s$ orbital and three $2p$ orbitals for carbon forms four hybrid orbitals, each with one electron. These new hybrid orbitals are intermediate in energy between the $2s$ and $2p$ orbitals.

Forming four sp^3 hybrid orbitals for carbon

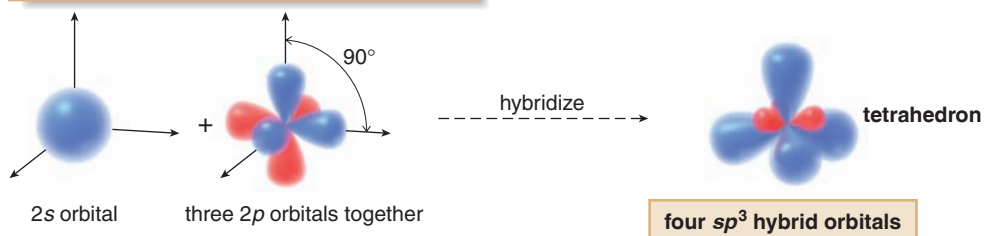


- These hybrid orbitals are called sp^3 hybrids because they are formed from *one* s orbital and *three* p orbitals.



What do these new hybrid orbitals look like? Mixing a spherical $2s$ orbital and three dumbbell-shaped $2p$ orbitals together produces four orbitals having one large lobe and one small lobe, oriented toward the corners of a tetrahedron. Each large lobe concentrates electron density in the bonding direction between two nuclei. This makes bonds formed from hybrid orbitals **stronger** than bonds formed from pure p orbitals.

Shape and orientation of sp^3 hybrid orbitals

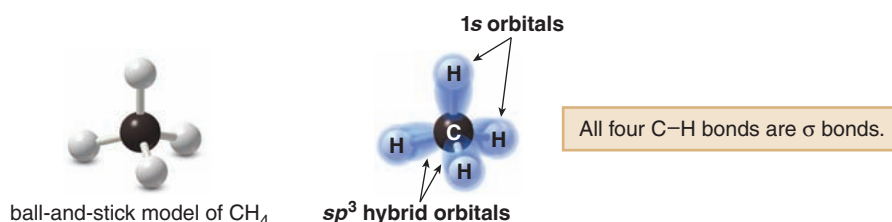


The four hybrid orbitals form four equivalent bonds. We can now explain the observed bonding in CH_4 .

- Each bond in CH_4 is formed by overlap of an sp^3 hybrid orbital of carbon with a $1s$ orbital of hydrogen. These four bonds point to the corners of a tetrahedron.

All four C–H bonds in methane are **σ bonds**, because the electron density is concentrated on the axis joining C and H. An orbital picture of the bonding in CH_4 is given in Figure 1.8.

Figure 1.8
Bonding in CH_4 using sp^3 hybrid orbitals



Problem 1.29 What orbitals are used to form each of the C–C and C–H bonds in $\text{CH}_3\text{CH}_2\text{CH}_3$ (propane)? How many σ bonds are present in this molecule?

1.8C Other Hybridization Patterns— sp and sp^2 Hybrid Orbitals

Forming sp^3 hybrid orbitals is just one way that $2s$ and $2p$ orbitals can hybridize. In fact, three common modes of hybridization are seen in organic molecules. The number of orbitals is always conserved in hybridization; that is, a **given number of atomic orbitals hybridize to form an equivalent number of hybrid orbitals**.

- One $2s$ orbital and *three* $2p$ orbitals form *four* sp^3 hybrid orbitals.
- One $2s$ orbital and *two* $2p$ orbitals form *three* sp^2 hybrid orbitals.
- One $2s$ orbital and *one* $2p$ orbital form *two* sp hybrid orbitals.

We have already seen pictorially how four sp^3 hybrid orbitals are formed from one $2s$ and three $2p$ orbitals. Figures 1.9 and 1.10 illustrate the same process for sp and sp^2 hybrids. Each sp and sp^2 hybrid orbital has one large and one small lobe, much like an sp^3 hybrid orbital. Note, however, that both sp^2 and sp hybridization **leave one and two $2p$ orbitals unhybridized**, respectively, on each atom.

The **superscripts** for hybrid orbitals correspond to the **number of atomic orbitals** used to form them. The number “1” is understood.

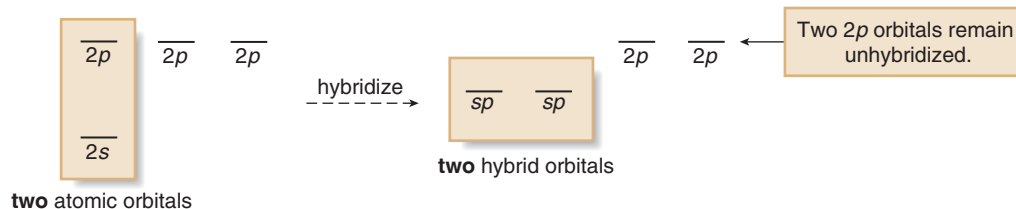
For example: $sp^3 = s^1p^3$

one $2s$ + **three** $2p$ orbitals
used to make each
hybrid orbital

number of groups around an atom	number of orbitals used	type of hybrid orbital
2	2	two sp hybrid orbitals
3	3	three sp^2 hybrid orbitals
4	4	four sp^3 hybrid orbitals

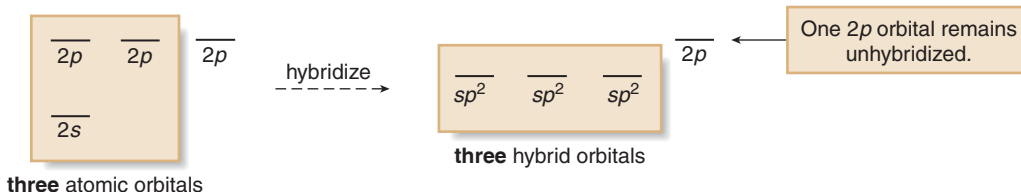
Let's illustrate this phenomenon with BeH_2 , BF_3 , NH_3 , and H_2O . We already determined the geometry in these molecules by counting groups in Section 1.6.

Figure 1.9
Forming two sp hybrid orbitals



- Forming **two sp hybrid orbitals** uses **one $2s$** and **one $2p$ orbital**, leaving **two $2p$ orbitals unhybridized**.

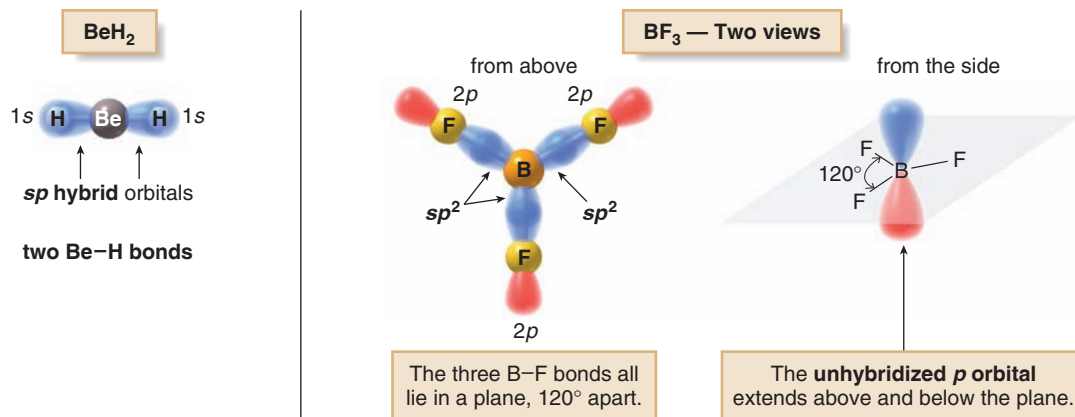
Figure 1.10
Forming three sp^2 hybrid orbitals



- Forming **three sp^2 hybrid orbitals** uses **one $2s$** and **two $2p$ orbitals**, leaving **one $2p$ orbital unhybridized**.

In BeH_2 , the **Be atom is sp hybridized** because it is surrounded by two groups (two H atoms). Each Be–H bond is formed by overlap of an sp hybrid orbital from Be and a $1s$ orbital from H. The sp hybrid orbitals are oriented 180° away from each other.

In BF_3 , the **B atom is sp^2 hybridized** because it is surrounded by three groups (three F atoms). Each B–F bond is formed by overlap of an sp^2 hybrid orbital from B and a $2p$ orbital from F. The sp^2 hybrid orbitals all lie in a plane, and are oriented 120° apart. The B atom also has a vacant unhybridized $2p$ orbital. This orbital is located **above and below the plane** of the BF_3 molecule.



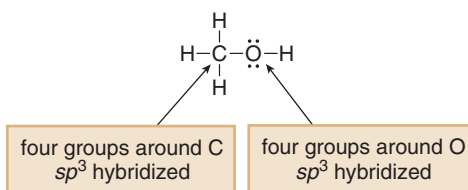
The N atom in NH_3 and the O atom in H_2O are both surrounded by four groups, making them sp^3 hybridized. Each N–H and O–H bond in these molecules is formed by overlap of an sp^3 hybrid orbital with a $1s$ orbital from H. The lone pairs of electrons on N and O also occupy sp^3 hybrid orbitals, as shown in Figure 1.11.

Sample Problem 1.9

What orbitals are used to form each bond in methanol, CH_3OH ?

Solution

To solve this problem, draw a valid Lewis structure and count groups around each atom. Then, use the rule to determine hybridization: two groups = sp , three groups = sp^2 , and four groups = sp^3 .



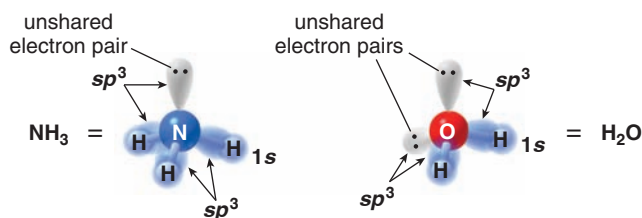
- All C–H bonds are formed from $\text{C}_{sp^3} - \text{H}_{1s}$.
- The C–O bond is formed from $\text{C}_{sp^3} - \text{O}_{sp^3}$.
- The O–H bond is formed from $\text{O}_{sp^3} - \text{H}_{1s}$.

Problem 1.30

What orbitals are used to form each bond in the following molecules?

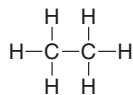
- a. CH_3BeH b. $(\text{CH}_3)_3\text{B}$ c. CH_3OCH_3

Figure 1.11
Hybrid orbitals of NH_3 and H_2O



1.9 Ethane, Ethylene, and Acetylene

Let's now use the principles of hybridization to determine the type of bonds in **ethane**, **ethylene**, and **acetylene**.



ethane



ethylene

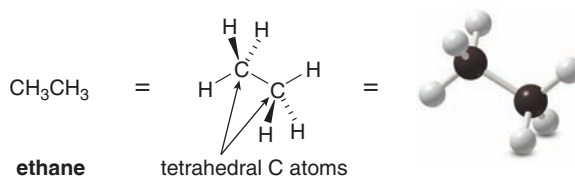


acetylene

1.9A Ethane—CH₃CH₃

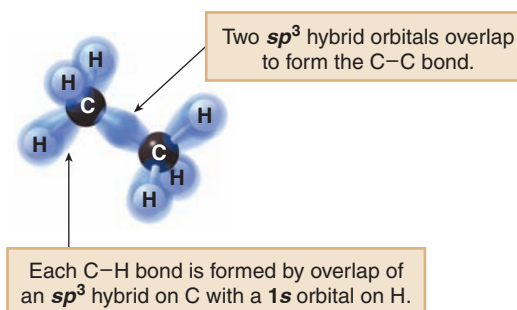
According to the Lewis structure for **ethane**, **CH₃CH₃**, each carbon atom is singly bonded to four other atoms. As a result:

- Each carbon is tetrahedral.
- Each carbon is sp^3 hybridized.

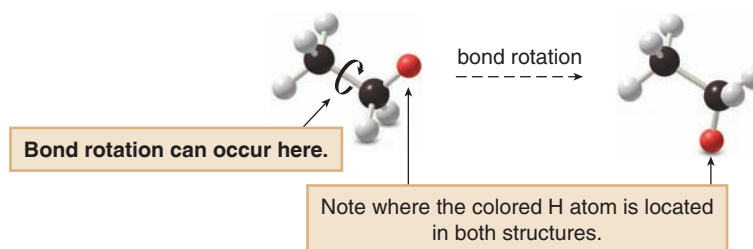


Ethane is a constituent of natural gas.

All of the bonds in ethane are σ bonds. The C–H bonds are formed from the overlap of one of the three sp^3 hybrid orbitals on each carbon atom with the $1s$ orbital on hydrogen. The C–C bond is formed from the overlap of an sp^3 hybrid orbital on each carbon atom.



Finally, a model of ethane shows that **rotation can occur around the central C–C σ bond**. Note how the relative position of the H atoms on the adjacent CH₃ groups changes from one representation to another. This process is discussed in greater detail in Chapter 4.



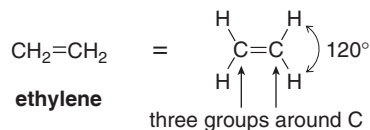
1.9B Ethylene—C₂H₄

Based on the Lewis structure of **ethylene**, **CH₂=CH₂**, each carbon atom is singly bonded to two H atoms and doubly bonded to the other C atom, so each C is surrounded by three groups. As a result:



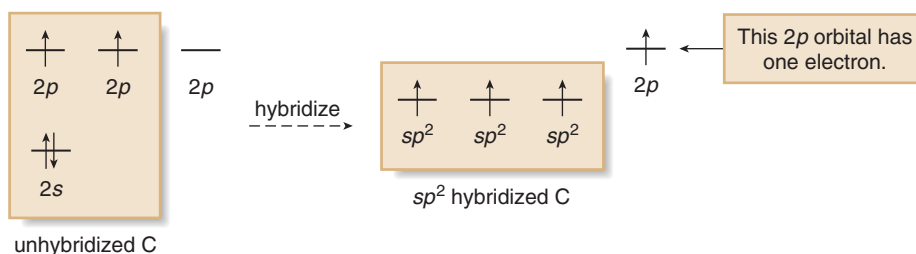
Ethylene is an important starting material in the preparation of the plastic polyethylene.

- Each carbon is trigonal planar (Section 1.6B).
- Each carbon is sp^2 hybridized.

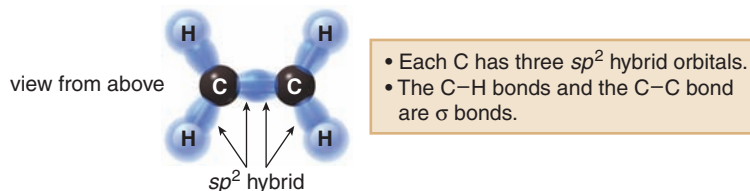


What orbitals are used to form the two bonds of the C–C double bond? Recall from Section 1.8 that sp^2 hybrid orbitals are formed from **one 2s and two 2p orbitals**, leaving one **2p orbital unhybridized**. Because carbon has four valence electrons, **each of these orbitals has one electron** that can be used to form a bond.

Forming an sp^2 hybridized carbon atom

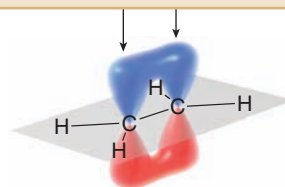


Each C–H bond results from the end-on overlap of an sp^2 hybrid orbital on carbon and the $1s$ orbital on hydrogen. Similarly, one of the C–C bonds results from the end-on overlap of an sp^2 hybrid orbital on each carbon atom. Each of these bonds is a **σ bond**.



The second C–C bond results from the side-by-side overlap of the 2p orbitals on each carbon. Side-by-side overlap creates an area of electron density above and below the plane containing the sp^2 hybrid orbitals (that is, the plane containing the six atoms in the σ bonding system).

Overlap of the 2p orbitals forms the second C–C bond.



In this second bond, the electron density is **not** concentrated on the axis joining the two nuclei. This new type of bond is called a **π bond**. Because the electron density in a π bond is farther from the two nuclei, **π bonds are usually weaker and therefore more easily broken than σ bonds**.

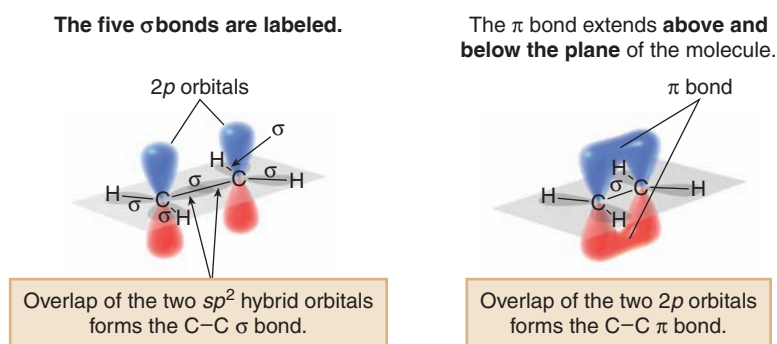
Thus, a carbon–carbon double bond has two components:

- a σ bond, formed by end-on overlap of two sp^2 hybrid orbitals;
- a π bond, formed by side-by-side overlap of two 2p orbitals.

Figure 1.12 summarizes the bonding observed in ethylene.

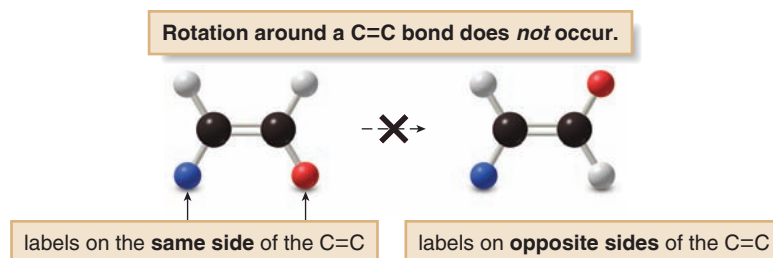
Figure 1.12

Summary: The σ and π bonds in ethylene



Unlike the C–C single bond in ethane, rotation about the C–C double bond in ethylene is **restricted**. It can occur only if the π bond first breaks and then re-forms, a process that requires considerable energy.

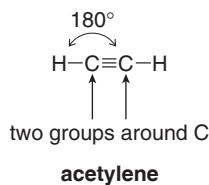
All double bonds are composed of one σ and one π bond.



1.9C Acetylene— C_2H_2

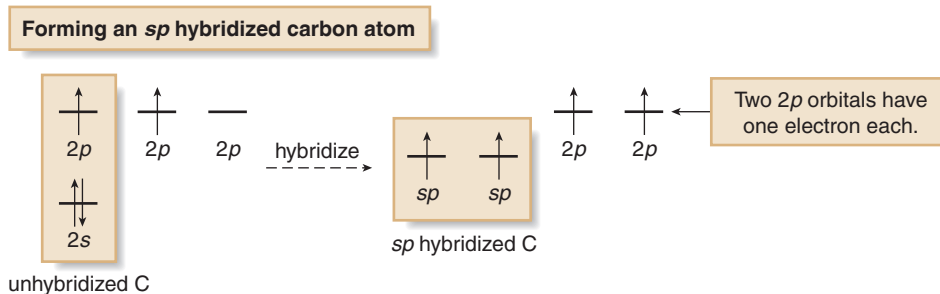
Based on the Lewis structure of **acetylene**, $HC\equiv CH$, each carbon atom is singly bonded to one hydrogen atom and triply bonded to the other carbon atom, so each carbon atom is surrounded by two groups. As a result:

- Each carbon is linear (Section 1.6B).
- Each carbon is sp hybridized.

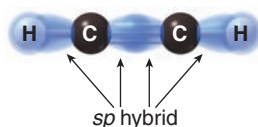


Because acetylene produces a very hot flame on burning, it is often used in welding torches. The fire is very bright, too, so it was once used in the lamps worn by spelunkers—people who study and explore caves.

What orbitals are used to form the bonds of the C–C triple bond? Recall from Section 1.8 that sp hybrid orbitals are formed from **one $2s$ and one $2p$ orbital**, leaving **two $2p$ orbitals unhybridized**. Because carbon has four valence electrons, **each of these orbitals has one electron** that can be used to form a bond.

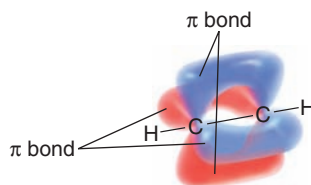


Each C–H bond results from the end-on overlap of an sp hybrid orbital on carbon and the $1s$ orbital on hydrogen. Similarly, one of the C–C bonds results from the end-on overlap of an sp hybrid orbital on each carbon atom. Each of these bonds is a σ bond.



- Each C has two sp hybrid orbitals.
- The C–H bonds and C–C bond are σ bonds.

Each carbon atom also has two **unhybridized $2p$ orbitals** that are perpendicular to each other and to the sp hybrid orbitals. Side-by-side overlap between the two $2p$ orbitals on one carbon with the two $2p$ orbitals on the other carbon creates the second and third bonds of the C–C triple bond. The electron density from one of these two bonds is above and below the axis joining the two nuclei, and the electron density from the second of these two bonds is in front of and behind the axis, so both of these bonds are π bonds.



The side-by-side overlap of two p orbitals always forms a π bond.

All triple bonds are composed of one σ and two π bonds.

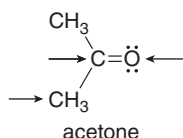
Thus, a carbon–carbon triple bond has three components:

- a σ bond, formed by end-on overlap of two sp hybrid orbitals;
- two π bonds, formed by side-by-side overlap of two sets of $2p$ orbitals.

Figure 1.13 summarizes the bonding observed in acetylene. Figure 1.14 summarizes the three possible types of bonding in carbon compounds.

Sample Problem 1.10

Answer each question for the molecule acetone, drawn below:



- Determine the hybridization of the indicated atoms.
- What orbitals are used to form the C–O double bond?
- In what type of orbital does each lone pair reside?

Solution

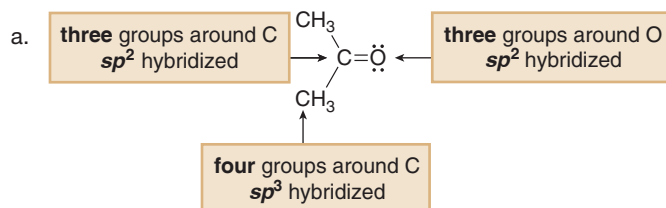
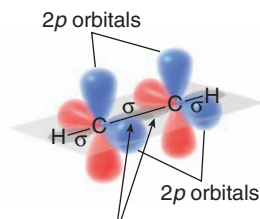


Figure 1.13

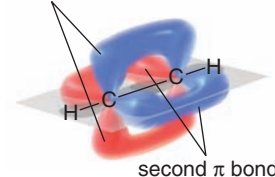
Summary: The σ and π bonds in acetylene

The three σ bonds are labeled.



Overlap of the two sp hybrid orbitals forms the C–C σ bond.

Two π bonds extend out from the axis of the linear molecule. one π bond


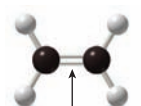
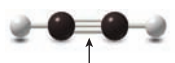


second π bond

Overlap of two sets of two $2p$ orbitals forms two C–C π bonds.

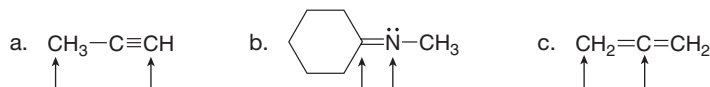
Figure 1.14

A summary of covalent bonding seen in carbon compounds

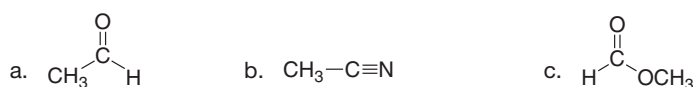
Number of groups bonded to C	Hybridization	Bond angle	Example	Observed bonding
4	sp^3	109.5°	CH_3CH_3 ethane	 one σ bond $\text{C}_{sp^3}-\text{C}_{sp^3}$
3	sp^2	120°	$\text{CH}_2=\text{CH}_2$ ethylene	 one σ bond + one π bond $\text{C}_{sp^2}-\text{C}_{sp^2}$ $\text{C}_{2p}-\text{C}_{2p}$
2	sp	180°	$\text{HC}\equiv\text{CH}$ acetylene	 one σ bond + two π bonds $\text{C}_{sp}-\text{C}_{sp}$ $\text{C}_{2p}-\text{C}_{2p}$ $\text{C}_{2p}-\text{C}_{2p}$

- The σ bond is formed from the end-on overlap of $\text{C}_{sp^2}-\text{O}_{sp^2}$.
- The π bond is formed from the side-by-side overlap of $\text{C}_{2p}-\text{O}_{2p}$.
- c. The O atom has three sp^2 hybrid orbitals.
 - One is used for the σ bond of the double bond.
 - The remaining two sp^2 hybrids are occupied by the lone pairs.

Problem 1.31 Determine the hybridization around the indicated atoms in the following molecules:



Problem 1.32 Classify each bond in the following molecules as σ or π :

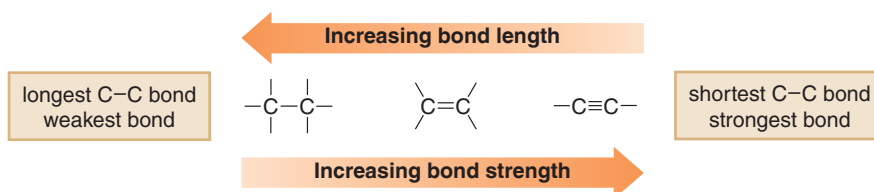


1.10 Bond Length and Bond Strength

Let's now examine the relative bond length and bond strength of the C–C and C–H bonds in ethane, ethylene, and acetylene.

1.10A A Comparison of Carbon–Carbon Bonds

While the SI unit of energy is the **joule** (J), organic chemists often report energy values in **calories** (cal). For this reason, energy values in the tables in this text are reported in joules, followed by the number of calories in parentheses. 1 cal = 4.18 J



- As the number of electrons between two nuclei *increases*, bonds become shorter and stronger.





Note the inverse relationship between bond length and bond strength. The shorter the bond, the closer the electron density is kept to the nucleus, and the harder the bond is to break.

Shorter bonds are stronger bonds.

- Thus, triple bonds are shorter and stronger than double bonds, which are shorter and stronger than single bonds.

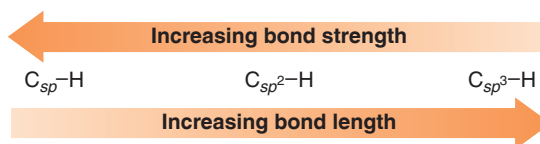
Values for bond lengths and bond strengths for CH_3CH_3 , $\text{CH}_2=\text{CH}_2$ and $\text{HC}\equiv\text{CH}$ are listed in Table 1.3. Be careful not to confuse two related but different principles regarding multiple bonds such as C–C double bonds. **Double bonds, consisting of both a σ and a π bond, are strong.** The π component of the double bond, however, is usually much *weaker* than the σ component. This is a particularly important consideration when studying alkenes in Chapter 10.

Table 1.3 Bond Lengths and Bond Strengths for Ethane, Ethylene, and Acetylene

Compound	C–C bond length (pm)	Bond strength kJ/mol (kcal/mol)
$\text{CH}_3\text{—CH}_3$	153	368 (88)
$\text{CH}_2=\text{CH}_2$	134	635 (152)
$\text{HC}\equiv\text{CH}$	121	837 (200)
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>Increasing bond length</p> </div> <div style="text-align: center;">  <p>Increasing bond strength</p> </div> </div>		
Compound	C–H bond length (pm)	Bond strength kJ/mol (kcal/mol)
$\text{CH}_3\text{CH}_2\text{—H}$	111	410 (98)
$\text{CH}_2=\text{C—H}$	110	435 (104)
$\text{HC}\equiv\text{C—H}$	109	523 (125)
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>Increasing bond length</p> </div> <div style="text-align: center;">  <p>Increasing bond strength</p> </div> </div>		

1.10B A Comparison of Carbon–Hydrogen Bonds

The length and strength of a C–H bond vary slightly depending on the hybridization of the carbon atom.



To understand why this is so, we must look at the atomic orbitals used to form each type of hybrid orbital. A single $2s$ orbital is always used, but the number of $2p$ orbitals varies with the type of hybridization. A quantity called **percent s -character** indicates the fraction of a hybrid orbital due to the $2s$ orbital used to form it.

$$sp \text{ hybrid} \quad \frac{\text{one } 2s \text{ orbital}}{\text{two hybrid orbitals}} = 50\% \text{ } s\text{-character}$$

$$sp^2 \text{ hybrid} \quad \frac{\text{one } 2s \text{ orbital}}{\text{three hybrid orbitals}} = 33\% \text{ } s\text{-character}$$

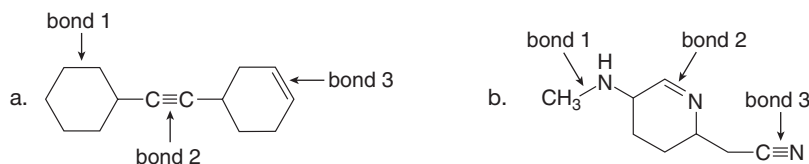
$$sp^3 \text{ hybrid} \quad \frac{\text{one } 2s \text{ orbital}}{\text{four hybrid orbitals}} = 25\% \text{ } s\text{-character}$$

Why should the percent s -character of a hybrid orbital affect the length of a C–H bond? A $2s$ orbital keeps electron density closer to a nucleus compared to a $2p$ orbital. As the **percent**

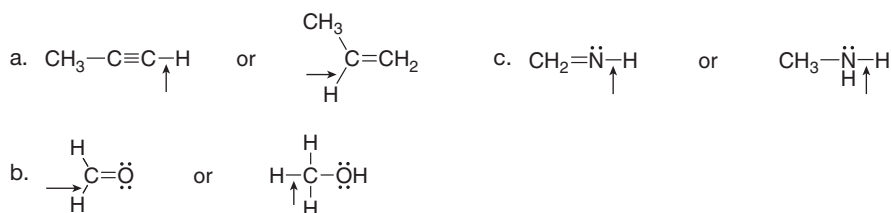
s-character increases, a hybrid orbital holds its electrons closer to the nucleus, and the **bond becomes shorter and stronger**.

Increased percent s-character \longrightarrow Increased bond strength \longrightarrow Decreased bond length

Problem 1.33 Rank the indicated bonds in each compound in order of (a) increasing bond strength and (b) increasing bond length.



Problem 1.34 Which of the indicated bonds in each pair of compounds is shorter?



1.11 Electronegativity and Bond Polarity

Electronegativity is a measure of an atom's attraction for electrons in a bond. Thus, electronegativity indicates how much a particular atom “wants” electrons. The following trends in electronegativity are observed in the periodic table:


- Electronegativity *increases* across a row of the periodic table as the nuclear charge increases (excluding the noble gases).
- Electronegativity *decreases* down a column of the periodic table as the atomic radius increases, pushing the valence electrons farther from the nucleus.


As a result, the *most* electronegative elements are located at the **upper right-hand corner** of the periodic table, and the *least* electronegative elements in the **lower left-hand corner**. A scale has been established to represent electronegativity values arbitrarily, from 0 to 4, as shown in Figure 1.15.

Electronegativity values are relative, so they can be used for comparison purposes only. When comparing two different elements, one is **more electronegative** than the other if it attracts elec-

Figure 1.15

Electronegativity values for some common elements

Increasing electronegativity 									
1A									
H 2.2	2A	//		3A	4A	5A	6A	7A	
Li 1.0	Be 1.6	//		B 1.8	C 2.5	N 3.0	O 3.4	F 4.0	
Na 0.9	Mg 1.3			Si 1.9	P 2.2	S 2.6	Cl 3.2		
K 0.8							Br 3.0		
							I 2.7		

 Increasing electronegativity

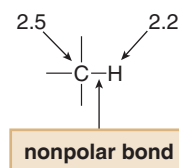
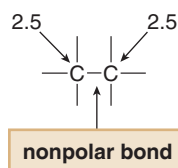
tron density toward itself. One is less electronegative—**more electropositive**—if it gives up electron density to the other element.

Problem 1.35

Rank the following atoms in order of increasing electronegativity. Label the most electronegative and most electropositive atom in each group.

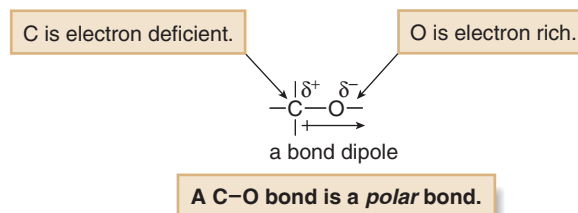
- a. Se, O, S b. P, Na, Cl c. Cl, S, F d. O, P, N

Electronegativity values are used as a guideline to indicate whether the electrons in a bond are **equally shared** or **unequally shared** between two atoms. For example, whenever two identical atoms are bonded together, each atom attracts the electrons in the bond to the same extent. The electrons are equally shared, and the **bond is nonpolar**. Thus, a **carbon–carbon bond is nonpolar**. The same is true whenever two different atoms having similar electronegativities are bonded together. **C–H bonds are considered to be nonpolar**, because the electronegativity difference between C (2.5) and H (2.2) is small.



The small electronegativity difference between C and H is ignored.

Bonding between atoms of different electronegativity values results in the **unequal sharing** of electrons. For example, in a C–O bond, the electrons are pulled away from C (2.5) toward O (3.4), the element of higher electronegativity. **The bond is polar, or polar covalent**. The bond is said to have a **dipole**; that is, a **separation of charge**.



The direction of polarity in a bond is often indicated by an arrow, with the head of the arrow pointing toward the more electronegative element. The tail of the arrow, with a perpendicular line drawn through it, is positioned at the less electronegative element. Alternatively, the symbols δ^+ and δ^- indicate this unequal sharing of electron density.

- δ^+ means an atom is electron deficient (has a partial positive charge).
- δ^- means the atom is electron rich (has a partial negative charge).

Problem 1.36

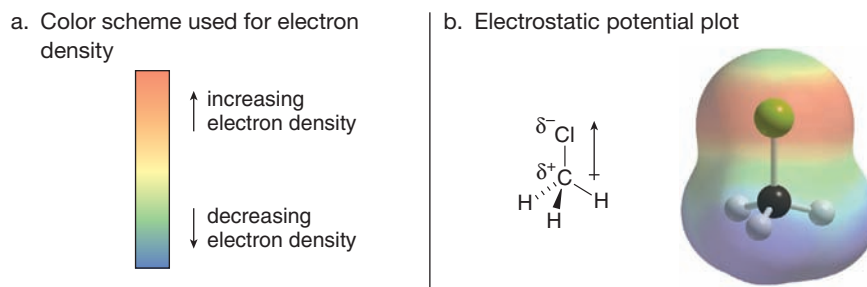
Show the direction of the dipole in each bond. Label the atoms with δ^+ and δ^- .

- a. H–F b. $\text{—}\overset{\text{H}}{\underset{\text{H}}{\text{B}}}\text{—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—}$ c. $\text{—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—Li}$ d. $\text{—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—Cl}$

Students often wonder how large an electronegativity difference must be to consider a bond polar. That's hard to say. We will set an arbitrary value for this difference and use it as an *approximation*. **Usually, a polar bond will be one in which the electronegativity difference between two atoms is ≥ 0.5 units.**

The distribution of electron density in a molecule can be shown using an **electrostatic potential map**. These maps are color coded to illustrate areas of high and low electron density. Electron-rich

Figure 1.16
Electrostatic potential
plot of CH_3Cl



regions are indicated in red, and electron-deficient sites are indicated in blue. Regions of intermediate electron density are shown in orange, yellow, and green.

For example, an electrostatic potential map of CH_3Cl clearly indicates the polar nature of the C–Cl bond (Figure 1.16). The more electronegative Cl atom pulls electron density toward it, making it electron rich. This is indicated by the red around the Cl in the plot. The carbon is electron deficient, and this is shown with blue.

When comparing two maps, the comparison is useful only if they are plotted *using the same scale* of color gradation. For this reason, whenever we compare two plots in this text, they will be drawn side by side using the same scale. It will be difficult to compare two plots in different parts of the book, because the scale may be different. Despite this limitation, an electrostatic potential plot is a useful tool for visually evaluating the distribution of electron density in a molecule, and with care, comparing the electron density in two different molecules.

1.12 Polarity of Molecules

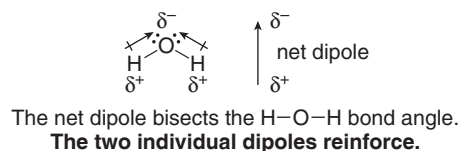
A **polar molecule** has either one polar bond, or two or more bond dipoles that reinforce. A **nonpolar molecule** has either no polar bonds, or two or more bond dipoles that cancel.

Whenever C or H is bonded to N, O, and all halogens, the bond is **polar**. Thus, the C–I bond is considered polar even though the electronegativity difference between C and I is small. Remember, electronegativity is just an approximation.

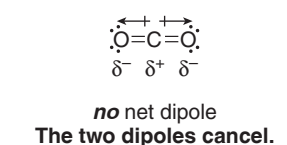
Thus far, we have been concerned with the polarity of one bond. To determine whether a molecule has a net dipole, use the following two-step procedure:

- [1] Use electronegativity differences to **identify all of the polar bonds and the directions of the bond dipoles**.
- [2] **Determine the geometry** around individual atoms by counting groups, and decide if individual dipoles **cancel** or **reinforce each other in space**.

The two molecules H_2O and CO_2 illustrate different outcomes of this process. In H_2O , each O–H bond is polar because the electronegativity difference between O (3.4) and H (2.2) is large. Since H_2O is a **bent** molecule, the two dipoles reinforce (both point *up*). Thus, **H_2O has a net dipole, making it a polar molecule**. CO_2 also has polar C–O bonds because the electronegativity difference between O (3.4) and C (2.5) is large. However, CO_2 is a **linear** molecule, so the two dipoles, which are equal and opposite in direction, **cancel**. Thus, **CO_2 is a nonpolar molecule with no net dipole**.



H_2O is a polar molecule.



CO_2 is a nonpolar molecule.

Electrostatic potential plots for H_2O and CO_2 appear in Figure 1.17. Additional examples of polar and nonpolar molecules are given in Figure 1.18.

Problem 1.37

Indicate which of the following molecules is polar because it possesses a net dipole. Show the direction of the net dipole if one exists.



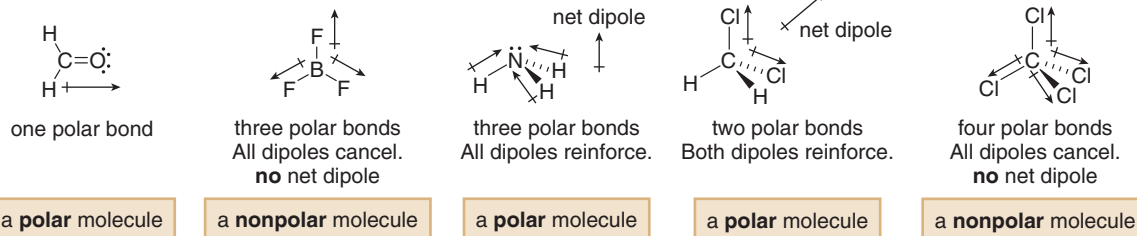
Figure 1.17

Electrostatic potential plots for H_2O and CO_2 

- The electron-rich (red) region is concentrated on the electronegative O atom. Both H atoms are electron deficient (blue-green).
- Both electronegative O atoms are electron rich (red) and the central C atom is electron deficient (blue).

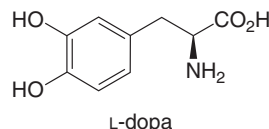
Figure 1.18

More examples of polar and nonpolar molecules



1.13 L-Dopa—A Representative Organic Molecule

The principles learned in this chapter apply to all organic molecules regardless of size or complexity. For example, we now know a great deal about the structure of **L-dopa**, a drug used to treat Parkinson's disease described in the chapter opener.

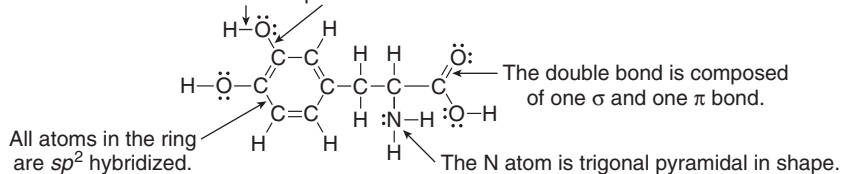


For example, you should be able to do all of the following:

- Convert this skeletal structure of L-dopa to a Lewis structure.
- Determine the hybridization and geometry around every atom.
- Label all polar and nonpolar bonds.
- Compare bond length and bond strength for certain bonds.

Some of these concepts are illustrated in the Lewis structure for L-dopa. As we continue our study of organic chemistry you will see that these fundamental properties about a molecule determine its physical properties and its behavior in chemical reactions.

The C—O and O—H bonds are polar.



Lewis structure of L-dopa

Problem 1.38

Provide the following information about L-dopa. In all cases, label different sites than those identified in the structure shown.

- Label two polar and two nonpolar bonds.
- Label all sp^3 hybridized C atoms.
- Label all H atoms that bear a partial positive charge (δ^+).
- Draw another resonance structure.

KEY CONCEPTS

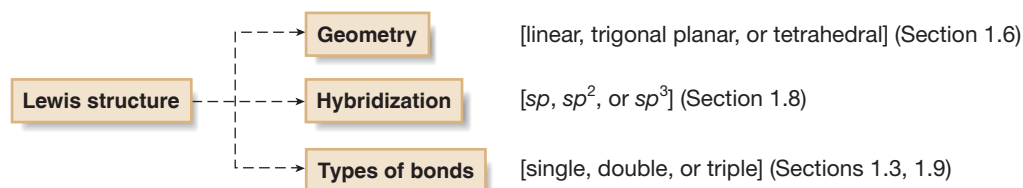
Structure and Bonding

Important Facts

- **The general rule of bonding:** Atoms “strive” to attain a complete outer shell of valence electrons (Section 1.2). H “wants” two electrons. Second-row elements “want” eight electrons.
- **Formal charge** is the difference between the number of valence electrons of an atom and the number of electrons it “owns” (Section 1.3C). See Sample Problem 1.4 for a stepwise example.
- **Curved arrow notation** shows the movement of an electron pair. The tail of the arrow always begins at an electron pair, either in a bond or a lone pair. The head points to where the electron pair “moves” (Section 1.5).
- **Electrostatic potential plots** are color-coded maps of electron density, indicating electron-rich and electron-deficient regions (Section 1.11).

The Importance of Lewis Structures (Sections 1.3, 1.4)

A properly drawn Lewis structure shows the number of bonds and lone pairs present around each atom in a molecule. In a valid Lewis structure, each H has two electrons, and each second-row element has no more than eight. This is the first step needed to determine many properties of a molecule.



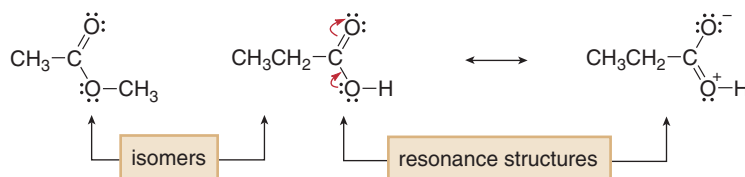
Resonance (Section 1.5)

The basic principles:

- Resonance exists when a compound cannot be represented by a single Lewis structure.
- Resonance structures differ in the position of only nonbonded electrons and π bonds, not atoms.
- The resonance hybrid is the only accurate representation for a resonance-stabilized compound. A hybrid represents the compound better than any single resonance structure because electron density is delocalized.

The difference between resonance structures and isomers:

- Two **isomers** differ in the arrangement of *both* atoms and electrons.
- **Resonance structures** differ *only* in the arrangement of electrons.



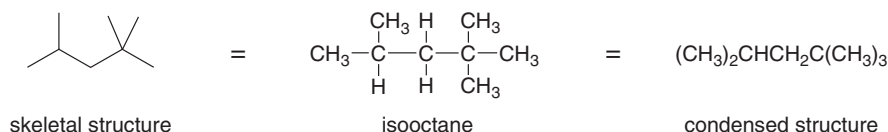
Geometry and Hybridization

The number of groups around an atom determines both its geometry (Section 1.6) and hybridization (Section 1.8).

Number of groups	Geometry	Bond angle ($^\circ$)	Hybridization
2	linear	180	sp
3	trigonal planar	120	sp^2
4	tetrahedral	109.5	sp^3

Drawing Organic Molecules (Section 1.7)

- Shorthand methods are used to abbreviate the structure of organic molecules.



- A carbon bonded to four atoms is tetrahedral. The best way to represent a tetrahedron is to draw two bonds in the plane, one bond in front, and one bond behind.

Bond Length

- Bond length decreases across a row and increases down a column of the periodic table (Section 1.6A).
- Bond length decreases as the number of electrons between two nuclei increases (Section 1.10A).
- Bond length decreases as the percent s-character increases (Section 1.10B).
- Bond length and bond strength are inversely related. In general, shorter bonds are stronger bonds (Section 1.10).
- Sigma (σ) bonds are generally stronger than π bonds (Section 1.9).

Electronegativity and Polarity (Sections 1.11, 1.12)

- Electronegativity increases across a row and decreases down a column of the periodic table.
- A polar bond results when two atoms of different electronegativity values are bonded together. Whenever C or H is bonded to N, O, or any halogen, the bond is polar.
- A polar molecule has either one polar bond, or two or more bond dipoles that reinforce.

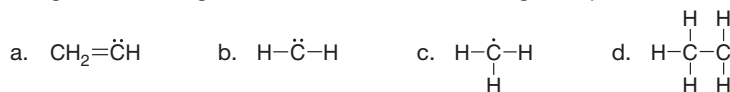
PROBLEMS

Atomic Structure, Ionic Bonding, and Covalent Bonding

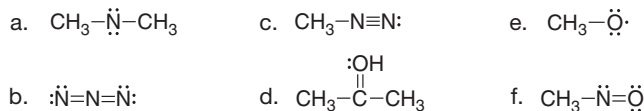
- 1.39** Two radioactive isotopes of iodine used for the diagnosis and treatment of thyroid disease have mass numbers of 123 and 131. For each isotope, give the following information: (a) the number of protons; (b) the number of neutrons; (c) the number of electrons in the neutral atom; (d) the group number.
- 1.40** Label each bond in the following compounds as ionic or covalent.
- a. NaI b. BrCl c. HCl d. CH_3NH_2 e. NaOCH_3

Lewis Structures and Formal Charge

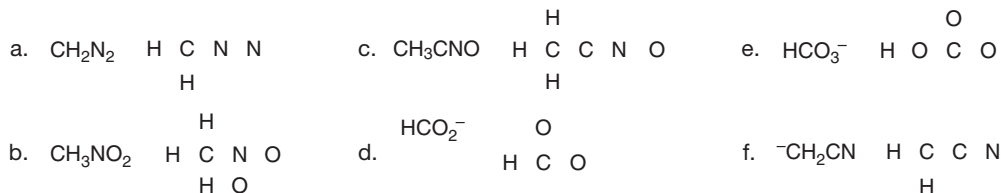
- 1.41** Assign formal charges to each carbon atom in the given species. All lone pairs have been drawn in.



- 1.42** Assign formal charges to each N and O atom in the given molecules. All lone pairs have been drawn in.



- 1.43** Draw one valid Lewis structure for each compound. Assume the atoms are arranged as drawn.



- 1.44** Draw a valid Lewis structure for each compound.



- 1.45** Draw an acceptable Lewis structure from each condensed structure, such that all atoms have zero formal charge.
- diethyl ether, $(\text{CH}_3\text{CH}_2)_2\text{O}$, the first general anesthetic used in medical procedures
 - acrylonitrile, CH_2CHCN , starting material used to manufacture synthetic Orlon fibers
 - dihydroxyacetone, $(\text{HOCH}_2)_2\text{CO}$, an ingredient in sunless tanning products
 - acetic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$, a reagent used to synthesize aspirin

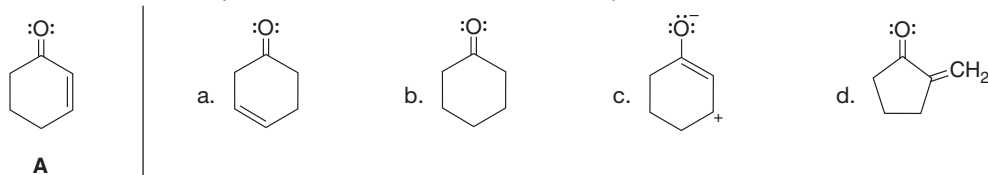
Isomers and Resonance Structures

- 1.46** Draw all possible isomers for each molecular formula.

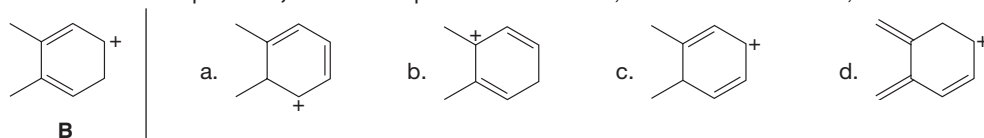
- $\text{C}_3\text{H}_7\text{Cl}$ (two isomers)
- $\text{C}_2\text{H}_4\text{O}$ (three isomers)
- $\text{C}_3\text{H}_9\text{N}$ (four isomers)

- 1.47** Draw Lewis structures for the nine isomers having molecular formula $\text{C}_3\text{H}_6\text{O}$, with all atoms having a zero formal charge.

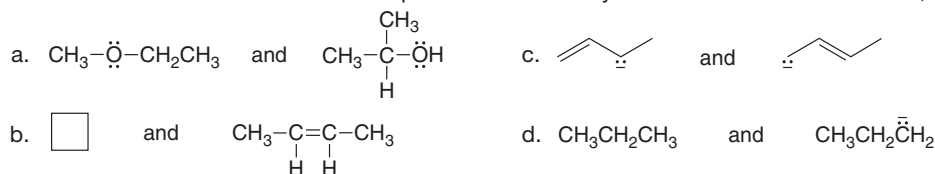
- 1.48** With reference to compound **A** drawn below, label each compound as an isomer, a resonance structure, or neither.



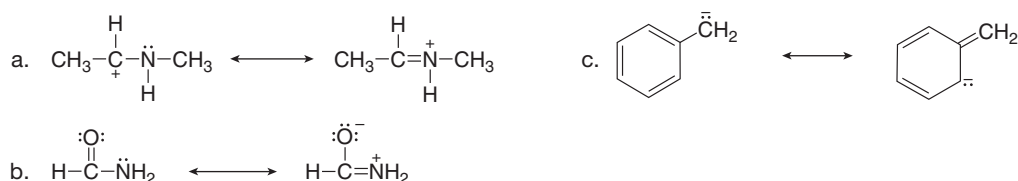
- 1.49** With reference to species **B**, label each species as an isomer, a resonance structure, or neither.



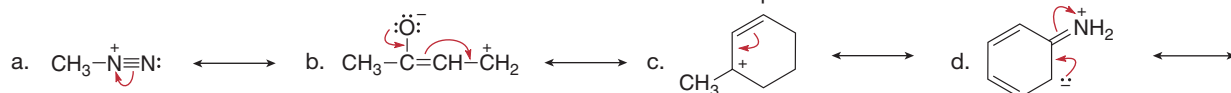
- 1.50** How are the molecules or ions in each pair related? Classify them as resonance structures, isomers, or neither.



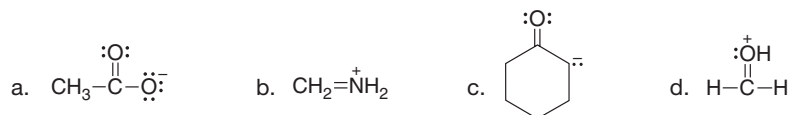
- 1.51** Add curved arrows to show how the first resonance structure can be converted into the second.



- 1.52** Follow the curved arrows to draw a second resonance structure for each species.

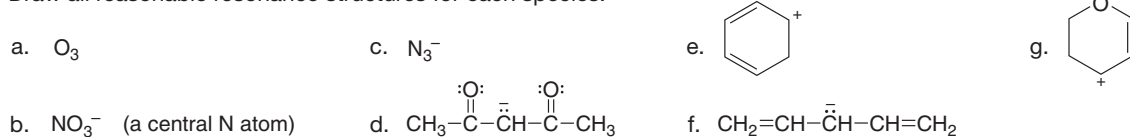


- 1.53** Draw a second resonance structure for each ion.

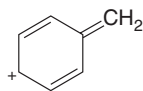


- 1.54** For each ion in Problem 1.53 draw the resonance hybrid.

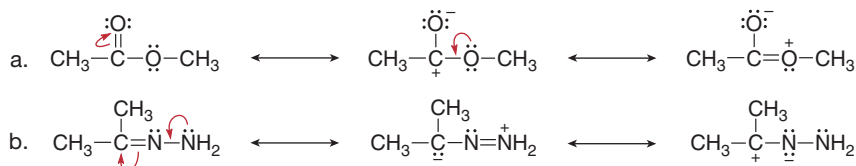
- 1.55** Draw all reasonable resonance structures for each species.



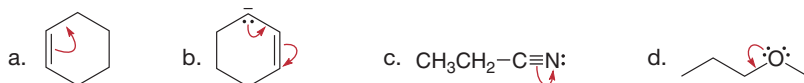
1.56 Draw four additional resonance structures for the following cation. Then draw the resonance hybrid.



1.57 Rank the resonance structures in each group in order of increasing contribution to the resonance hybrid. Label the resonance structure that contributes the most as **3** and the resonance structure that contributes the least as **1**. Label the intermediate contributor as **2**.

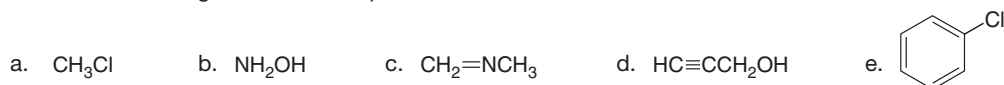


1.58 Consider the compounds and ions with curved arrows drawn below. When the curved arrows give a second valid resonance structure, draw the resonance structure. When the curved arrows generate an invalid Lewis structure, explain why the structure is unacceptable.

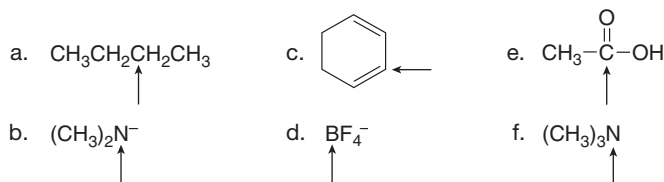


Geometry

1.59 Predict all bond angles in each compound.



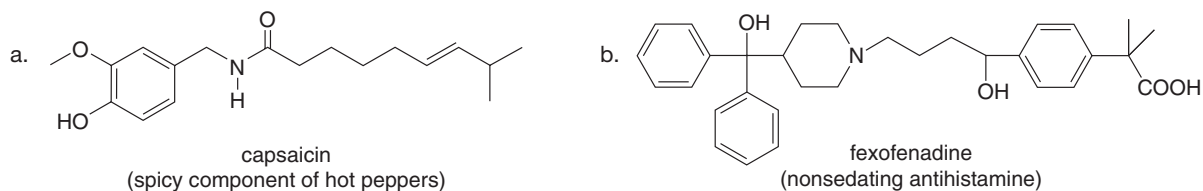
1.60 Predict the geometry around each indicated atom.



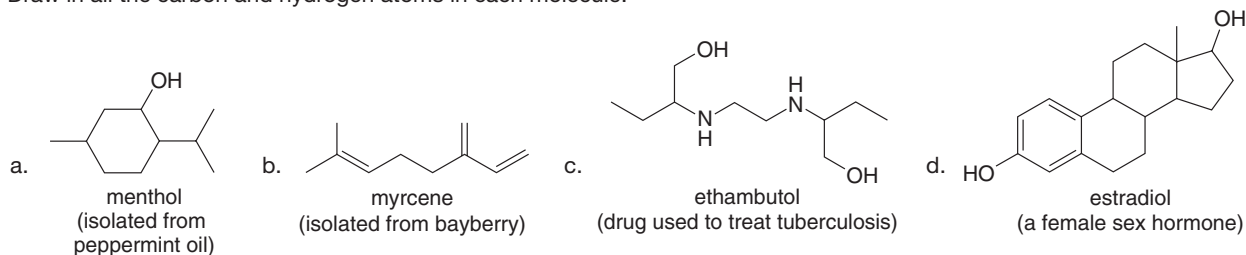
1.61 Draw the structure of halothane, CF_3CHClBr , in three dimensions, using solid lines, wedges, and dashes to illustrate the position of atoms. Halothane is a safe and widely used general anesthetic.

Drawing Organic Molecules

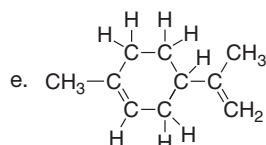
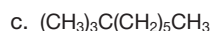
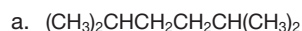
1.62 How many hydrogens are present around each carbon atom in the following molecules?



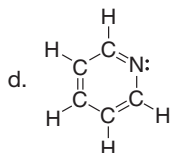
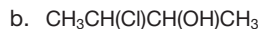
1.63 Draw in all the carbon and hydrogen atoms in each molecule.



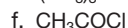
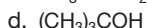
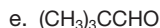
1.64 Convert each molecule into a skeletal structure.



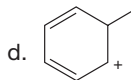
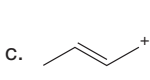
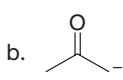
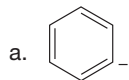
limonene
(oil of lemon)



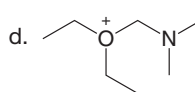
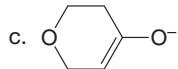
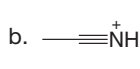
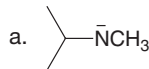
1.65 Convert the following condensed formulas into Lewis structures.



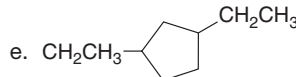
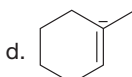
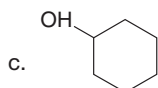
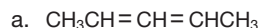
1.66 Draw in all the hydrogen atoms and nonbonded electron pairs in each ion.



1.67 Draw in all H atoms and lone pairs in each ion.

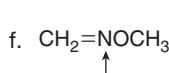
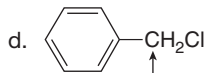
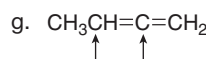
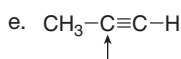
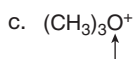
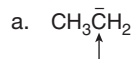


1.68 Each of the following condensed or skeletal structures is an incorrect representation of a molecule or ion. Explain what is wrong in each structure.

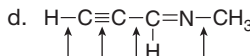
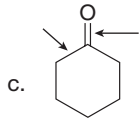
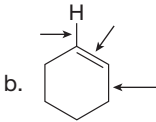
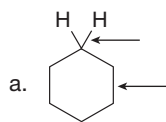


Hybridization

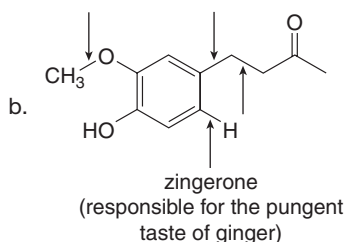
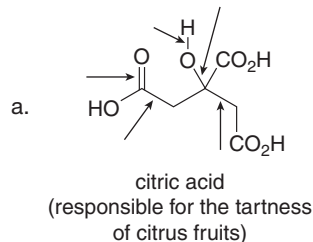
1.69 Predict the hybridization and geometry around each indicated atom.



1.70 What orbitals are used to form each indicated bond? For multiple bonds, indicate the orbitals used in individual bonds.

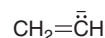
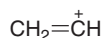


1.71 Citric acid and zingerone are two naturally occurring compounds. What orbitals are used to form each indicated bond?



1.72 Ketene, $\text{CH}_2=\text{C}=\text{O}$, is an unusual organic molecule that has a single carbon atom doubly bonded to two different atoms. Determine the hybridization of both C atoms and the O in ketene. Then, draw a diagram showing what orbitals are used to form each bond (similar to Figures 1.12 and 1.13).

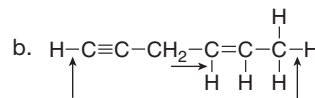
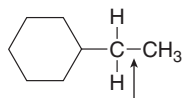
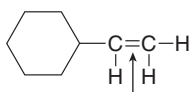
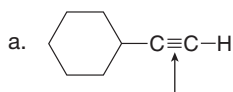
1.73 Consider the unstable cation and anion drawn below.



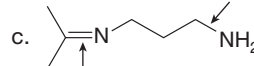
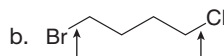
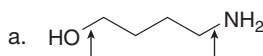
- What is the hybridization of each carbon atom in these ions?
- What orbitals are used to form both bonds in each carbon-carbon double bond?

Bond Length and Strength

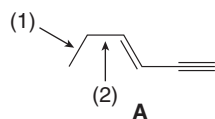
1.74 Rank the following bonds in order of *increasing* bond length.



1.75 Indicate the longer labeled bond in each compound.



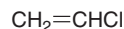
1.76 Answer the following questions about compound **A**.



- Label the shortest C-C single bond.
- Label the longest C-C single bond.
- Considering all the bonds, label the shortest C-C bond.
- Label the weakest C-C bond.
- Label the strongest C-H bond.
- Explain why bond (1) and bond (2) are different in length, even though they are both C-C single bonds.

1.77 A σ bond formed from two sp^2 hybridized C atoms is stronger than a σ bond formed from two sp^3 hybridized C atoms. Explain.

1.78 Two useful organic compounds that contain Cl atoms are drawn below. Vinyl chloride is the starting material used to prepare poly(vinyl chloride), a plastic used in insulation, pipes, and bottles. Chloroethane (ethyl chloride) is a local anesthetic. Why is the C-Cl bond of vinyl chloride stronger than the C-Cl bond in chloroethane?



vinyl chloride



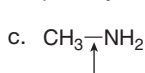
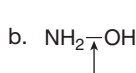
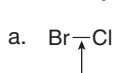
chloroethane
(ethyl chloride)

Bond Polarity

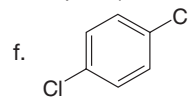
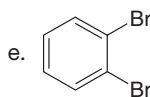
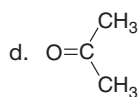
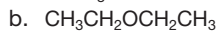
1.79 Answer each question with a brief explanation and an example to illustrate your answer.

- Can a compound be nonpolar if it contains one polar bond?
- Can a compound be nonpolar if it contains two or more polar bonds?
- Can a compound be polar if it contains no polar bonds?

1.80 Use the symbols δ^+ and δ^- to indicate the polarity of the labeled bonds.



1.81 Label the polar bonds in each molecule. Indicate the direction of the net dipole (if there is one).

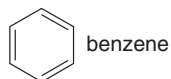


General Questions

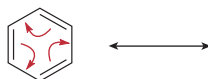
1.82 Answer the following questions about acetonitrile ($\text{CH}_3\text{C}\equiv\text{N}$).

- Determine the hybridization of both C atoms and the N atom.
- Label all bonds as σ or π .
- In what type of orbital does the lone pair on N reside?
- Label all bonds as polar or nonpolar.

1.83 Benzene is the simplest member of a whole class of compounds called aromatic hydrocarbons.

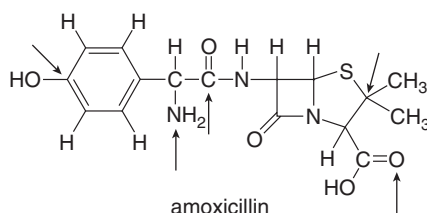


- How is each carbon atom hybridized?
- What is the geometry around each carbon atom? What is the overall geometry of the benzene ring?
- Draw a diagram showing the orbitals used to join the carbon atoms of the ring.
- Follow the indicated curved arrow notation to draw a second resonance structure.



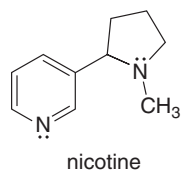
- Benzene and other aromatic hydrocarbons are shown in Chapter 17 to be very stable. Offer an explanation.

1.84 The principles of this chapter can be applied to organic molecules of any size. Answer the following questions about amoxicillin, an antibiotic from the penicillin family.



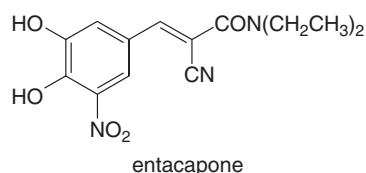
- Predict the hybridization and geometry around each indicated atom.
- Label five polar bonds using the symbols δ^+ and δ^- .
- Draw a skeletal structure.
- How many π bonds does amoxicillin have? Label them.
- Find a C-H bond containing a carbon atom having a hybrid orbital with 33% s-character.

1.85



- What is the hybridization of each N atom in nicotine?
- What is the geometry around each N atom?
- In what type of orbital does the lone pair on each N atom reside?
- Draw a constitutional isomer of nicotine.
- Draw a resonance structure of nicotine.

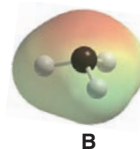
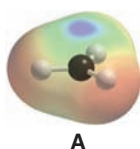
1.86 Stalevo is the trade name for a medication used for Parkinson's disease, which contains both L-dopa and entacapone.



- Draw a Lewis structure for entacapone.
- Which C-C bond in entacapone is the longest?
- Which C-C single bond is the shortest?
- Which C-N bond is the longest?
- Which C-N bond is the shortest?
- Use curved arrows to draw a resonance structure that is an equal contributor to the resonance hybrid.
- Use curved arrows to draw a resonance structure that is a minor contributor to the resonance hybrid.

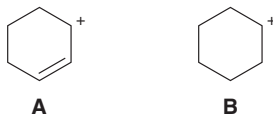
1.87 CH_3^+ and CH_3^- are two highly reactive carbon species.

- What is the predicted hybridization and geometry around each carbon atom?
- Two electrostatic potential plots are drawn for these species. Which ion corresponds to which diagram and why?

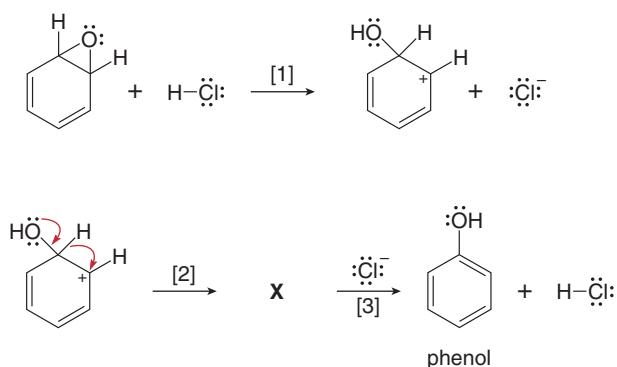


Challenge Problems

- 1.88 When two carbons having different hybridization are bonded together, the C–C bond contains a slight dipole. In a $C_{sp^2}-C_{sp^3}$ bond, what is the direction of the dipole? Which carbon is considered more electronegative?
- 1.89 Draw all possible isomers having molecular formula C_4H_8 that contain one π bond.
- 1.90 Use the principles of resonance theory to explain why carbocation **A** is more stable than carbocation **B**.



- 1.91 The curved arrow notation introduced in Section 1.5 is a powerful method used by organic chemists to show the movement of electrons not only in resonance structures, but also in chemical reactions. Since each curved arrow shows the movement of two electrons, following the curved arrows illustrates what bonds are broken and formed in a reaction. Consider the following three-step process. (a) Add curved arrows in Step [1] to show the movement of electrons. (b) Use the curved arrows drawn in Step [2] to identify the structure of **X**. **X** is converted in Step [3] to phenol and HCl.



2

Acids and Bases

- 2.1 Brønsted–Lowry acids and bases
- 2.2 Reactions of Brønsted–Lowry acids and bases
- 2.3 Acid strength and pK_a
- 2.4 Predicting the outcome of acid–base reactions
- 2.5 Factors that determine acid strength
- 2.6 Common acids and bases
- 2.7 Aspirin
- 2.8 Lewis acids and bases



Aspirin is one of the most widely used over-the-counter drugs. Whether you purchase Anacin, Bufferin, Bayer, or a generic, the active ingredient is the same—**acetylsalicylic acid**. Aspirin, a synthetic compound that does not occur in nature, was first marketed to the general public in 1899, and is now used regularly by over 100 million people throughout the world. Like many drugs, aspirin undergoes a proton transfer reaction after ingestion. In Chapter 2, we learn about acidity and the role of acid–base reactions in aspirin's chemistry.

Chemical terms such as *anion* and *cation* may be unfamiliar to most nonscientists, but *acid* has found a place in everyday language. Commercials advertise the latest remedy for the heartburn caused by excess stomach *acid*. The nightly news may report the latest environmental impact of *acid* rain. Wine lovers know that wine sours because its alcohol has turned to *acid*. *Acid* comes from the Latin word *acidus*, meaning sour, because when tasting compounds was a routine method of identification, these compounds were sour.

In Chapter 2, we will concentrate on two definitions of acids and bases: the **Brønsted–Lowry** definition, which describes acids as *proton donors* and bases as *proton acceptors*, and the **Lewis** definition, which describes acids as *electron pair acceptors* and bases as *electron pair donors*.

2.1 Brønsted–Lowry Acids and Bases

The general words “acid” and “base” usually mean a Brønsted–Lowry acid and Brønsted–Lowry base.

H^+ = proton

H–A = general Brønsted–Lowry acid.

B: = general Brønsted–Lowry base.

The Brønsted–Lowry definition describes acidity in terms of protons: positively charged **hydrogen ions, H^+** .

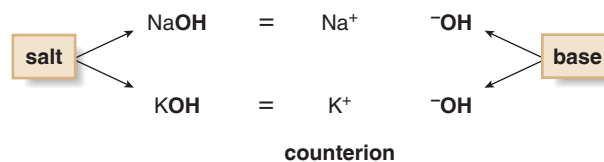
- A Brønsted–Lowry acid is a *proton donor*.
- A Brønsted–Lowry base is a *proton acceptor*.

A Brønsted–Lowry acid must contain a hydrogen atom. This definition of an acid is often familiar to students, because many inorganic acids in general chemistry are Brønsted–Lowry acids. The symbol **H–A** is used for a general Brønsted–Lowry acid.

A Brønsted–Lowry base must be able to form a bond to a proton. Because a proton has no electrons, a base must contain an “available” **electron pair** that can be easily donated to form a new bond. These include **lone pairs** or electron pairs in **π bonds**. The symbol **B:** is used for a general Brønsted–Lowry base.

Examples of Brønsted–Lowry acids and bases are given in Figure 2.1.

Charged species such as OH^- and NH_2^- are used as **salts**, with cations such as Li^+ , Na^+ , or K^+ to balance the negative charge. These cations are called **counterions** or **spectator ions**, and their **identity is usually inconsequential**. For this reason, the counterion is often omitted.



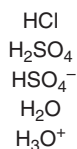
Compounds like H_2O and CH_3OH that contain both hydrogen atoms and lone pairs may be either an acid or a base, depending on the particular reaction. These fundamental principles are true no matter how complex the compound. For example, the addictive pain reliever **morphine** is a

Figure 2.1

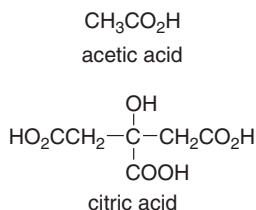
Examples of Brønsted–Lowry acids and bases

Brønsted–Lowry acids [H–A]

Inorganic



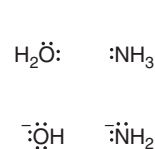
Organic



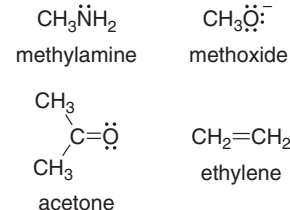
- All Brønsted–Lowry acids contain a proton.
- The net charge may be zero, (+), or (–).

Brønsted–Lowry bases [B:]

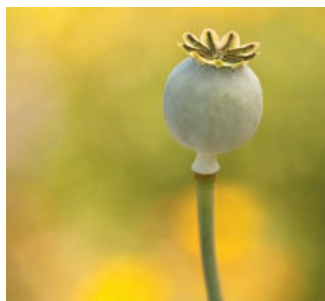
Inorganic



Organic

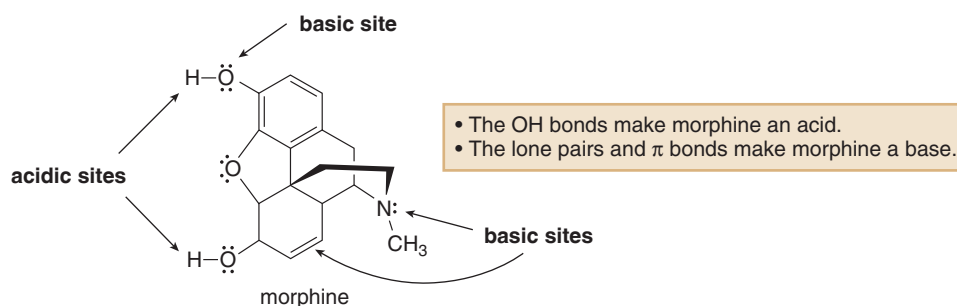


- All Brønsted–Lowry bases contain a lone pair of electrons or a π bond.
- The net charge may be zero or (–).



Morphine is obtained from the opium poppy.

Brønsted–Lowry acid because it contains many hydrogen atoms. It is also a Brønsted–Lowry base because it has lone pairs on O and N, and four π bonds.



Problem 2.1

- Which compounds are Brønsted–Lowry acids: HBr , NH_3 , CCl_4 ?
- Which compounds are Brønsted–Lowry bases: CH_3CH_3 , $(\text{CH}_3)_3\text{CO}^-$, $\text{HC}\equiv\text{CH}$?
- Classify each compound as an acid, a base, or both: $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CO}_2\text{CH}_3$.

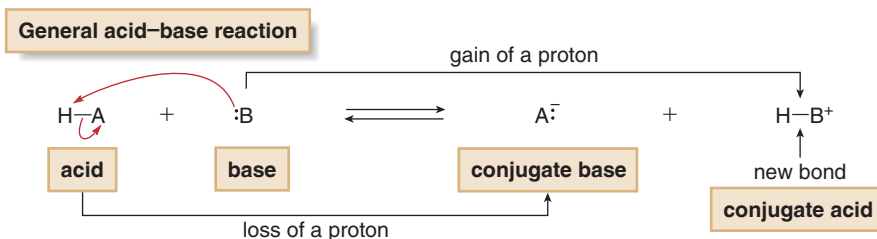
2.2 Reactions of Brønsted–Lowry Acids and Bases

A Brønsted–Lowry acid–base reaction results in transfer of a proton from an acid to a base. These acid–base reactions, also called *proton transfer reactions*, are fundamental to the study of organic chemistry.

Consider, for example, the reaction of the acid $\text{H}-\text{A}$ with the base $:\text{B}$. In an acid–base reaction, one bond is broken and one is formed.

- The electron pair of the base B : forms a new bond to the proton of the acid.
- The acid $\text{H}-\text{A}$ loses a proton, leaving the electron pair in the $\text{H}-\text{A}$ bond on A .

Recall from Section 1.5 that a curved arrow shows the movement of an **electron pair**. The tail of the arrow always begins at an electron pair and the head points to where that electron pair “moves.”



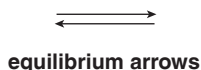
This “movement” of electrons in reactions can be illustrated using curved arrow notation. Because **two electron pairs** are involved in this reaction, **two curved arrows** are needed. Two products are formed.

- Loss of a proton from an acid forms its *conjugate base*.
- Gain of a proton by a base forms its *conjugate acid*.

Keep in mind two other facts about this general reaction:

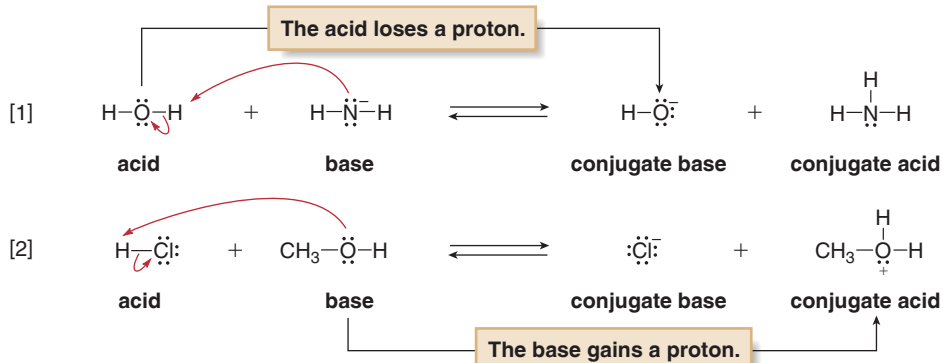
- The **net charge must be the same** on both sides of any equation. In this example, the net charge on each side is zero. Individual charges can be calculated using formal charges.
- A **double reaction arrow** is used between starting materials and products to indicate that the reaction can proceed in the forward and reverse directions. These are **equilibrium arrows**.

A double reaction arrow indicates equilibrium.



Remove H^+ from an acid to form its conjugate base.
Add H^+ to a base to form its conjugate acid.

Two examples of proton transfer reactions are drawn here with curved arrow notation.



- Brønsted–Lowry acid–base reactions always result in the transfer of a proton from an acid to a base.

The ability to identify and draw a conjugate acid or base from a given starting material is illustrated in Sample Problems 2.1 and 2.2.

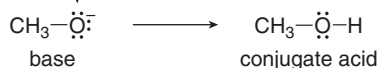
Sample Problem 2.1

- What is the conjugate acid of CH_3O^- ?
- What is the conjugate base of NH_3 ?

Solution

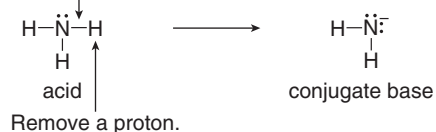
- Add H^+ to CH_3O^- to form its conjugate acid.

Add a proton to a lone pair.



- Remove H^+ from NH_3 to form its conjugate base.

Leave the electron pair on N.



Problem 2.2

- Draw the conjugate acid of each base: NH_3 , Cl^- , $(\text{CH}_3)_2\text{C}=\text{O}$.
- Draw the conjugate base of each acid: HBr , HSO_4^- , CH_3OH .

Problem 2.3

The presence of a π bond also makes a compound a base. With this in mind, draw the conjugate acid of ethylene, $\text{CH}_2=\text{CH}_2$. What is ethylene's conjugate base?

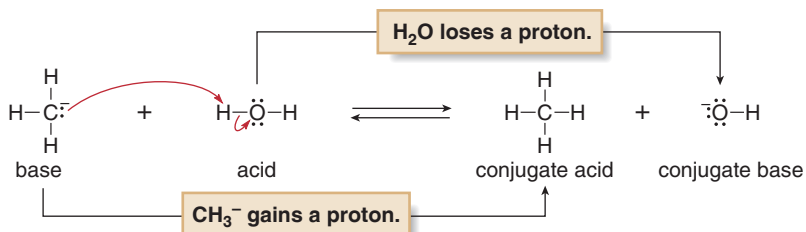
Sample Problem 2.2

Label the acid and base, and the conjugate acid and base in the following reaction. Use curved arrow notation to show the movement of electron pairs.

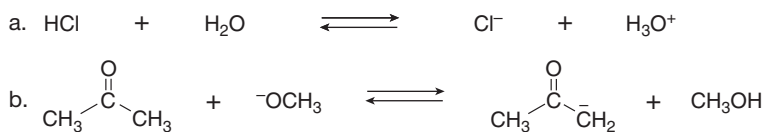


Solution

CH_3^- is the base because it accepts a proton, forming its conjugate acid, CH_4 . H_2O is the acid because it donates a proton, forming its conjugate base, ^-OH . Two curved arrows are needed. One shows that the lone pair on CH_3^- bonds to a proton of H_2O , and the second shows that the electron pair in the $\text{O}-\text{H}$ bond remains on O.



Problem 2.4 Label the acid and base, and the conjugate acid and base in the following reactions. Use curved arrows to show the movement of electron pairs.



In all proton transfer reactions, the **electron-rich base** donates an electron pair to the acid, which usually has a polar H–A bond. Thus, the H of the acid bears a partial positive charge, making it **electron deficient**. This is the first example of a general pattern of reactivity.

- Electron-rich species react with electron-deficient ones.

Given two starting materials, how do you know which is the acid and which is the base in a proton transfer reaction? The following generalizations will help to decide this in many reactions:

- [1] Common acids and bases introduced in general chemistry will often be used in the same way in organic reactions. HCl and H_2SO_4 are strong acids, and ^-OH is a strong base.
- [2] When only one starting material contains a hydrogen, it must be the acid. If only one starting material has a lone pair or a π bond, it must be the base.
- [3] A starting material with a net positive charge is usually the acid. A starting material with a negative charge is usually the base.

Problem 2.5 Draw the products of each proton transfer reaction.



Problem 2.6 Draw the products formed from the acid–base reaction of HCl with each compound.

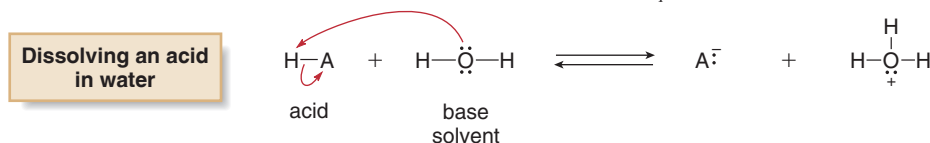


2.3 Acid Strength and $\text{p}K_a$

Acid strength is the tendency of an acid to donate a proton.

- The more readily a compound donates a proton, the stronger the acid.

Acidity is measured by an equilibrium constant. When a Brønsted–Lowry acid $\text{H}-\text{A}$ is dissolved in water, an acid–base reaction occurs, and an equilibrium constant K_{eq} can be written for the reaction.



Equilibrium constant

$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{starting materials}]} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}-\text{A}][\text{H}_2\text{O}]}$$

Because the concentration of the solvent H_2O is essentially constant, the equation can be rearranged and a new equilibrium constant, called the **acidity constant**, K_a , can be defined.

$$\text{Acidity constant} = K_a = [\text{H}_2\text{O}]K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}-\text{A}]}$$

How is the magnitude of K_a related to acid strength?

- The *stronger the acid*, the further the equilibrium lies to the right, and the *larger the K_a* .

For most organic compounds, K_a is small, typically 10^{-5} to 10^{-50} . This contrasts with the K_a values for many inorganic acids, which range from 10^0 to 10^{10} . Because dealing with exponents can be cumbersome, it is often more convenient to use pK_a values instead of K_a values.

Definition: $pK_a = -\log K_a$

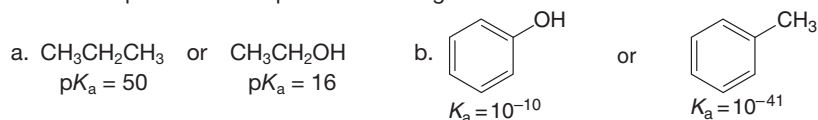
How does pK_a relate to acid strength?

Recall that a **log** is an **exponent**; for example, $\log 10^{-5} = -5$.

K_a	$pK_a = -\log K_a$
K_a values of typical organic acids	pK_a values of typical organic acids
10^{-5} to 10^{-50}	$+5$ to $+50$
larger number stronger acid	smaller number stronger acid
smaller number weaker acid	larger number weaker acid

- The *smaller the pK_a* , the *stronger the acid*.

Problem 2.7 Which compound in each pair is the stronger acid?



Problem 2.8 Use a calculator when necessary to answer the following questions.

- What is the pK_a for each K_a : 10^{-10} , 10^{-21} , and 5.2×10^{-5} ?
- What is the K_a for each pK_a : 7, 11, and 3.2?

Understanding acid strength is the first step to understanding base strength (and vice versa), because **an inverse relationship exists between acidity and basicity**.

- A *strong acid* readily donates a proton, forming a *weak conjugate base*.
- A *strong base* readily accepts a proton, forming a *weak conjugate acid*.

Table 2.1 is a brief list of pK_a values for some common compounds, ranked in order of **increasing pK_a** and therefore **decreasing acidity**. Because strong acids form weak conjugate bases, this list also ranks their conjugate bases, in order of **increasing basicity**. For example, CH_4 is the

Table 2.1 Selected pK_a Values

	Acid	pK_a	Conjugate base	
Increasing acidity of the acid ↑	H–Cl	–7	Cl^-	Increasing basicity of the conjugate base ↓
	$\text{CH}_3\text{COO–H}$	4.8	CH_3COO^-	
	HO–H	15.7	HO^-	
	$\text{CH}_3\text{CH}_2\text{O–H}$	16	$\text{CH}_3\text{CH}_2\text{O}^-$	
	$\text{HC}\equiv\text{CH}$	25	$\text{HC}\equiv\text{C}^-$	
	H–H	35	H^-	
	$\text{H}_2\text{N–H}$	38	H_2N^-	
	$\text{CH}_2=\text{CH}_2$	44	$\text{CH}_2=\text{CH}^-$	
	$\text{CH}_3\text{–H}$	50	CH_3^-	

weakest acid in the list, because it has the highest pK_a (50). Its conjugate base, CH_3^- , is therefore the strongest conjugate base. An extensive pK_a table is located in Appendix A.

Comparing pK_a values thus provides two useful bits of information: the **relative acidity of two acids**, and the **relative basicity of their conjugate bases**, as shown in Sample Problem 2.3.

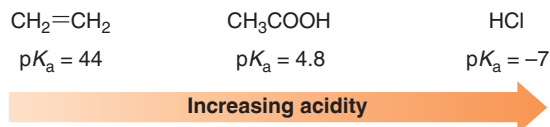
Sample Problem 2.3

Rank the following compounds in order of increasing acidity, and then rank their conjugate bases in order of increasing basicity.

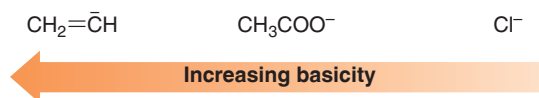


Solution

The pK_a values in Table 2.1 allow us to rank these compounds in order of increasing acidity: **the lower the pK_a , the stronger the acid**.



Because strong acids form weak conjugate bases, the **basicity of conjugate bases increases with increasing pK_a of their acids**.



Problem 2.9

Rank the conjugate bases of each group of acids in order of increasing basicity.

- a. NH_3 , H_2O , CH_4 b. $\text{CH}_2=\text{CH}_2$, $\text{HC}\equiv\text{CH}$, CH_4

Problem 2.10

Consider two acids: HCO_2H (formic acid, $pK_a = 3.8$) and pivalic acid [$(\text{CH}_3)_3\text{CCO}_2\text{H}$, $pK_a = 5.0$]. (a) Which acid has the larger K_a ? (b) Which acid is the stronger acid? (c) Which acid forms the stronger conjugate base? (d) When each acid is dissolved in water, for which acid does the equilibrium lie further to the right?

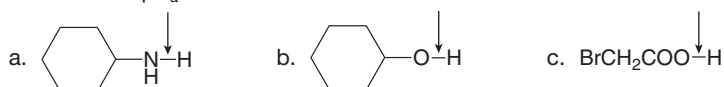
The pK_a values in Table 2.1 span a large range (-7 to 50). The **pK_a scale is logarithmic**, so a small difference in pK_a translates into a large numerical difference. For example, the difference between the pK_a of NH_3 (38) and $\text{CH}_2=\text{CH}_2$ (44) is six pK_a units. This means that NH_3 is 10^6 or **one million times more acidic** than $\text{CH}_2=\text{CH}_2$.

Although Table 2.1 is abbreviated, it gives pK_a values of many common compounds seen in organic chemistry. It is also a useful tool for *estimating* the pK_a of a compound similar though not identical to one in the table.

Suppose you are asked to estimate the pK_a of the $\text{N}-\text{H}$ bond of CH_3NH_2 . Although CH_3NH_2 is not listed in the table, we have enough information to *approximate* its pK_a . Because the pK_a of the $\text{N}-\text{H}$ bond of NH_3 is 38 , we can estimate the pK_a of the $\text{N}-\text{H}$ bond of CH_3NH_2 to be 38 . Its actual pK_a is 40 , so this is a good first approximation.

Problem 2.11

Estimate the pK_a of each of the indicated bonds.



2.4 Predicting the Outcome of Acid–Base Reactions

In a proton transfer reaction, the **stronger acid reacts with the stronger base** to form the weaker acid and the weaker base.

A proton transfer reaction represents an equilibrium. Because an acid donates a proton to a base, thus forming a conjugate acid and conjugate base, there are always two acids and two bases in the reaction mixture. Which pair of acids and bases is favored at equilibrium? **The position of the equilibrium depends on the relative strengths of the acids and bases.**

- Equilibrium always favors formation of the weaker acid and base.

Because a strong acid readily donates a proton and a strong base readily accepts one, these two species react to form a weaker conjugate acid and base that do not donate or accept a proton as readily. Comparing pK_a values allows us to determine the position of equilibrium, as illustrated in Sample Problem 2.4.

Sample Problem 2.4

Determine the direction of equilibrium when acetylene ($\text{HC}\equiv\text{CH}$) reacts with NH_2^- in a proton transfer reaction.

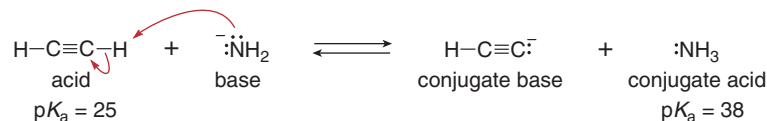
Solution

Follow three steps to determine the position of equilibrium:

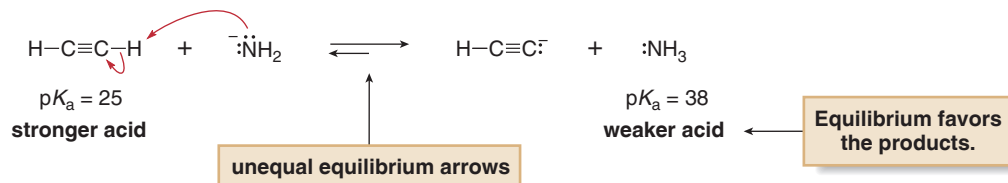
Step [1] Identify the acid and base in the starting materials.

- Assume NH_2^- is the base because it bears a net negative charge. That makes $\text{HC}\equiv\text{CH}$ the acid.

Step [2] Draw the products of proton transfer and identify the conjugate acid and base in the products.



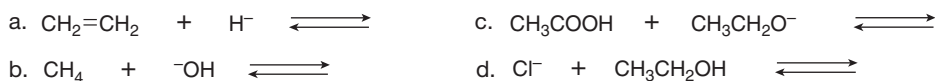
Step [3] Compare the pK_a values of the acid and the conjugate acid. Equilibrium favors formation of the weaker acid with the higher pK_a .



- Because the pK_a of the starting acid (25) is **lower** than the pK_a of the conjugate acid (38), $\text{HC}\equiv\text{CH}$ is a **stronger** acid and equilibrium favors the products.

Problem 2.12

Draw the products of each reaction and determine the direction of equilibrium.



How can we know if a particular base is strong enough to deprotonate a given acid, so that the equilibrium lies to the right? The pK_a table readily gives us this information.

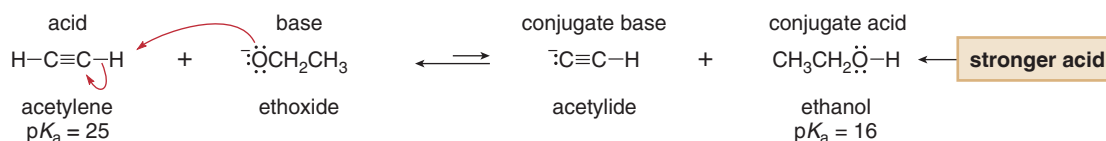
Compare any two entries in Table 2.1, such as ethanol ($\text{CH}_3\text{CH}_2\text{OH}$; $pK_a = 16$) and acetylene ($\text{HC}\equiv\text{CH}$; $pK_a = 25$), and their conjugate bases, ethoxide ($\text{CH}_3\text{CH}_2\text{O}^-$) and acetylide ($\text{HC}\equiv\text{C}^-$). Ethanol is a stronger acid than acetylene, so acetylide is a stronger base than ethoxide.

Because Table 2.1 is arranged from low to high pK_a , **an acid can be deprotonated by the conjugate base of any acid below it in the table.**

	acid	pK_a	conjugate base
stronger acid →	$\text{CH}_3\text{CH}_2\ddot{\text{O}}-\text{H}$ ethanol	16	$\text{CH}_3\text{CH}_2\ddot{\text{O}}^-$ ethoxide
	$\text{H}-\text{C}\equiv\text{C}-\text{H}$ acetylene	25	$\text{H}-\text{C}\equiv\text{C}^-$ ← stronger base
			acetylide

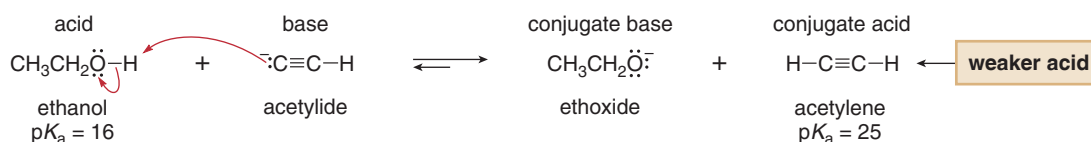
Two proton transfer reactions are possible.

- [1] Reaction of acetylene with ethoxide forms acetylide and ethanol. Because the stronger acid is the product of the reaction, *equilibrium favors the starting materials*. The base ethoxide is *not strong enough to deprotonate acetylene*.



Equilibrium favors the starting materials.

- [2] Reaction of ethanol with acetylide forms ethoxide and acetylene. Because the weaker acid is the product of the reaction, *equilibrium favors the products*. Thus, the base acetylide is *strong enough to deprotonate ethanol*.



Equilibrium favors the products.

In the second reaction, **ethanol is deprotonated by acetylide, the conjugate base of an acid weaker than itself**. This is a specific example of a general fact.

- An acid can be deprotonated by the conjugate base of any acid having a *higher* pK_a .

Problem 2.13

Answer the following questions by referring to Table 2.1:

- Which of the following bases is strong enough to deprotonate CH_3COOH : H^- , $\text{HC}\equiv\text{C}^-$, and Cl^- ?
- List four bases that are strong enough to deprotonate $\text{HC}\equiv\text{CH}$.

Problem 2.14

Using the data in Appendix A, determine which of the following bases is strong enough to deprotonate acetonitrile (CH_3CN) so that equilibrium favors the products: (a) NaH ; (b) Na_2CO_3 ; (c) NaOH ; (d) NaNH_2 ; (e) NaHCO_3 .

2.5 Factors That Determine Acid Strength

We have already learned in Section 2.3 that a tremendous difference in acidity exists among compounds. HCl ($pK_a < 0$) is an extremely strong acid. Water ($pK_a = 15.7$) is moderate in acidity, and CH_4 ($pK_a = 50$) is an extremely weak acid. How are these differences explained? There is one general rule.

- Anything that stabilizes a conjugate base A^- makes the starting acid $\text{H}-\text{A}$ more acidic.

For now we will concentrate on how structural differences between molecules can profoundly affect acidity. In Chapter 6, we will learn how to relate the stability of a species to its relative potential energy.

Four factors affect the acidity of $\text{H}-\text{A}$:

- [1] Element effects
- [2] Inductive effects
- [3] Resonance effects
- [4] Hybridization effects

No matter which factor is discussed, the same procedure is always followed. To compare the acidity of any two acids:

- Always draw the conjugate bases.
- Determine which conjugate base is more stable.
- The *more stable* the conjugate base, the *more acidic* the acid.

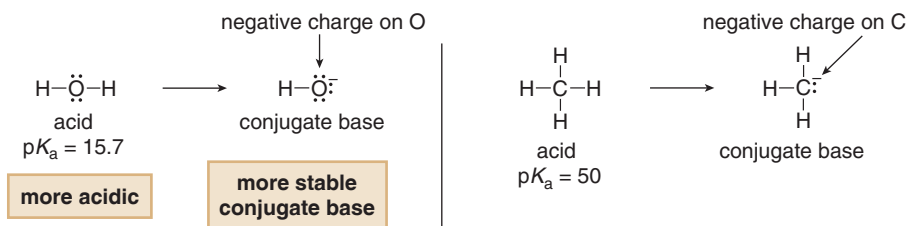
2.5A Element Effects—Trends in the Periodic Table

The most important factor determining the acidity of $\text{H}-\text{A}$ is the location of A in the periodic table.

Comparing Elements in the Same Row of the Periodic Table

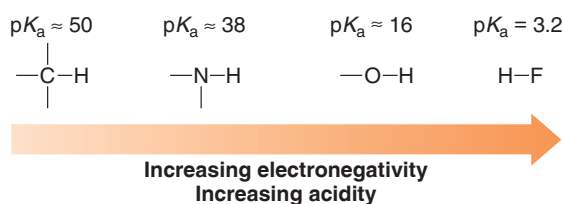
Examine acidity trends **across a row** of the periodic table by comparing CH_4 and H_2O , two compounds having H atoms bonded to a second-row element. We know from Table 2.1 that **H_2O has a much lower $\text{p}K_{\text{a}}$ and therefore is much more acidic than CH_4** , but why is this the case?

To answer this question, first draw both conjugate bases and then determine which is more stable. Each conjugate base has a net negative charge, but the negative charge in ^-OH is on oxygen and in CH_3^- it is on carbon.



Because the oxygen atom is much **more electronegative** than carbon, oxygen more readily accepts a negative charge, making ^-OH much more stable than CH_3^- . **H_2O is a stronger acid than CH_4 because ^-OH is a more stable conjugate base than CH_3^-** . This is a specific example of a general trend.

- Across a row of the periodic table, the acidity of $\text{H}-\text{A}$ increases as the electronegativity of A increases.



The enormity of this effect is evident by noting the approximate $\text{p}K_{\text{a}}$ values for these bonds. A **$\text{C}-\text{H}$ bond is approximately 10^{47} times less acidic than $\text{H}-\text{F}$** .

Comparing Elements Down a Column of the Periodic Table

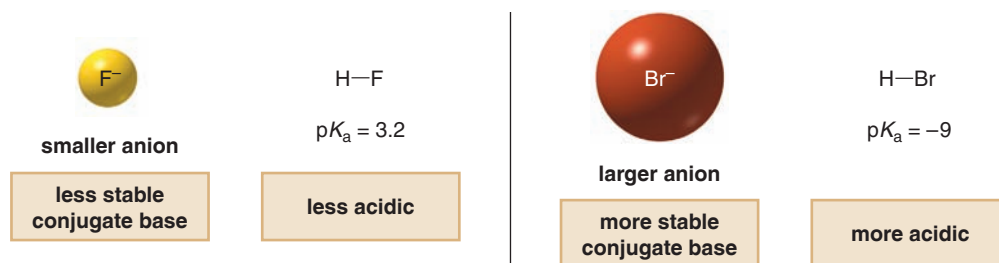
Now examine acidity trends down a column of the periodic table by comparing $\text{H}-\text{F}$ and $\text{H}-\text{Br}$. Once again, first draw both conjugate bases and then determine which is more stable. In this case, removal of a proton forms F^- and Br^- .



There are two important differences between F^- and Br^- —electronegativity and size. In this case, **size is more important than electronegativity**. The size of an atom or ion increases down a column of the periodic table, so Br^- is much larger than F^- , and this stabilizes the negative charge.

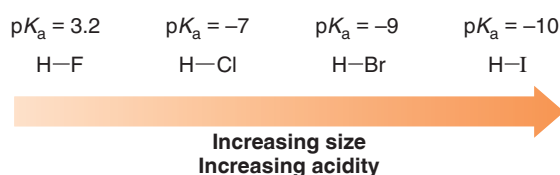
- Positive or negative charge is stabilized when it is spread over a larger volume.

Because Br^- is larger than F^- , Br^- is more stable than F^- , and $\text{H}-\text{Br}$ is a stronger acid than $\text{H}-\text{F}$.



This again is a specific example of a general trend.

- Down a column of the periodic table, the acidity of $\text{H}-\text{A}$ increases as the size of A increases.



Because of carbon's position in the periodic table (in the second row and to the left of O, N, and the halogens), **C-H bonds are usually the least acidic bonds in a molecule.**

This is *opposite* to what would be expected on the basis of electronegativity differences between F and Br, because F is more electronegative than Br. **Size and not electronegativity determines acidity down a column.** Combining both trends together:

- The acidity of $\text{H}-\text{A}$ increases both left-to-right across a row and down a column of the periodic table.

Sample Problem 2.5

Without reference to a $\text{p}K_{\text{a}}$ table, decide which compound in each pair is the stronger acid:

- a. H_2O or HF b. H_2S or H_2O

Solution

- a. H_2O and $\text{H}-\text{F}$ both have H atoms bonded to a second-row element. Because the acidity of $\text{H}-\text{A}$ increases across a row of the periodic table, the $\text{H}-\text{F}$ bond is more acidic than the $\text{H}-\text{O}$ bond. **HF is a stronger acid than H_2O .**
- b. H_2O and H_2S both have H atoms bonded to elements in the same column. Because the acidity of $\text{H}-\text{A}$ increases down a column of the periodic table, the $\text{H}-\text{S}$ bond is more acidic than the $\text{H}-\text{O}$ bond. **H_2S is a stronger acid than H_2O .**

Problem 2.15

Without reference to a $\text{p}K_{\text{a}}$ table, decide which compound in each pair is the stronger acid.

- a. NH_3 or H_2O b. HBr or HCl c. H_2S or HBr

Problem 2.16

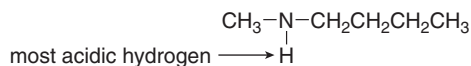
Which compound in each pair of isomers is the stronger acid?

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ or $(\text{CH}_3)_3\text{N}$ b. $\text{CH}_3\text{CH}_2\text{OCH}_3$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

When discussing acidity, the most acidic proton in a compound is the one removed first by a base. Although four factors determine the overall acidity of a particular hydrogen atom, **element effects—the identity of A—is the single most important factor in determining the acidity of the $\text{H}-\text{A}$ bond.**

To decide which hydrogen is most acidic, **first determine what element each hydrogen is bonded to and then decide its acidity based on periodic trends.** For example, $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

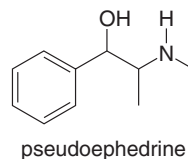
contains only C–H and N–H bonds. Since the acidity of H–A increases across a row of the periodic table, the single H on N is the most acidic H in this compound.



Problem 2.17 Which hydrogen in each molecule is most acidic?

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ b. $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ c. $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

Problem 2.18 Which hydrogen in pseudoephedrine, the nasal decongestant in the commercial medication Sudafed, is most acidic?

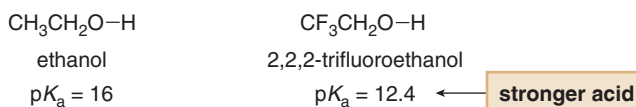


2.5B Inductive Effects



Because the pseudoephedrine (Problem 2.18) in Sudafed can be readily converted to the illegal, addictive drug methamphetamine, products that contain pseudoephedrine are now stocked behind the pharmacy counter so their sale can be more closely monitored. Sudafed PE is a related product that contains a decongestant less easily converted to methamphetamine.

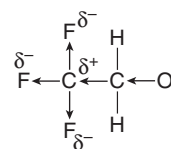
A second factor affecting the acidity of H–A is the presence of electronegative atoms. To illustrate this phenomenon, compare ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and 2,2,2-trifluoroethanol ($\text{CF}_3\text{CH}_2\text{OH}$), two different compounds containing O–H bonds. The $\text{p}K_a$ table in Appendix A indicates that $\text{CF}_3\text{CH}_2\text{OH}$ is a stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$. Because we are comparing the acidity of the O–H bond in both compounds, what causes the difference?



Once again first draw both conjugate bases and then determine which is more stable. Both bases have a negative charge on an electronegative oxygen, but the second anion has three additional electronegative fluorine atoms. These fluorine atoms withdraw electron density from the carbon to which they are bonded, making it electron deficient. Furthermore, this electron-deficient carbon pulls electron density through σ bonds from the negatively charged oxygen atom, stabilizing the negative charge. This is called an **inductive effect**.



No additional electronegative atoms stabilize the conjugate base.



CF_3 withdraws electron density, stabilizing the conjugate base.

- An *inductive effect* is the pull of electron density through σ bonds caused by electronegativity differences of atoms.

In this case, the electron density is pulled away from the negative charge through σ bonds by the very electronegative fluorine atoms, and so it is called an **electron-withdrawing inductive effect**. Thus, the three electronegative fluorine atoms stabilize the negatively charged conjugate base $\text{CF}_3\text{CH}_2\text{O}^-$, making $\text{CF}_3\text{CH}_2\text{OH}$ a stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$. We have learned two important principles from this discussion:

- More electronegative atoms stabilize regions of high electron density by an electron-withdrawing inductive effect.
- The acidity of H–A increases with the presence of electron-withdrawing groups in A.

Figure 2.2

Electrostatic potential plots of $\text{CH}_3\text{CH}_2\text{O}^-$ and $\text{CF}_3\text{CH}_2\text{O}^-$



Inductive effects result because an electronegative atom stabilizes the negative charge of the conjugate base. **The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.** This effect is discussed in greater detail in Chapter 19.

Electrostatic potential plots in Figure 2.2 compare the electron density around the oxygen atoms in these conjugate bases. The darker red around the O atom of $\text{CH}_3\text{CH}_2\text{O}^-$ indicates a higher concentration of electron density compared to the O atom of $\text{CF}_3\text{CH}_2\text{O}^-$.

Problem 2.19

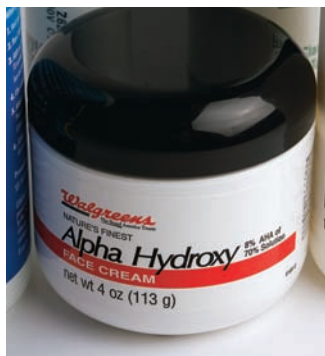
Which compound in each pair is the stronger acid?

- a. ClCH_2COOH or FCH_2COOH c. CH_3COOH or $\text{O}_2\text{NCH}_2\text{COOH}$
 b. $\text{Cl}_2\text{CHCH}_2\text{OH}$ or $\text{Cl}_2\text{CHCH}_2\text{CH}_2\text{OH}$

Problem 2.20

Glycolic acid, $\text{HOCH}_2\text{CO}_2\text{H}$, is the simplest member of a group of compounds called α -hydroxy acids, ingredients in skin care products that have an OH group on the carbon adjacent to a CO_2H group. Would you expect $\text{HOCH}_2\text{CO}_2\text{H}$ to be a stronger or weaker acid than acetic acid, $\text{CH}_3\text{CO}_2\text{H}$?

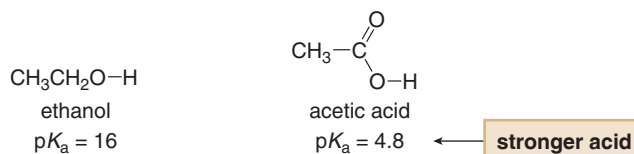
2.5C Resonance Effects



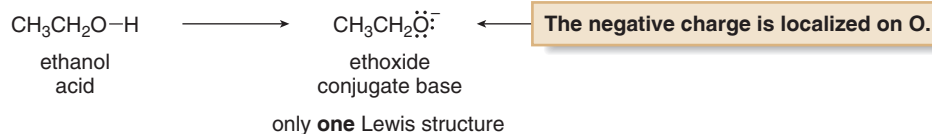
α -Hydroxy acids (Problem 2.20) are used in skin care products that purportedly smooth fine lines and improve skin texture by reacting with the outer layer of skin cells, causing them to loosen and flake off.

Recall that resonance structures are two Lewis structures having the same placement of atoms but a different arrangement of electrons.

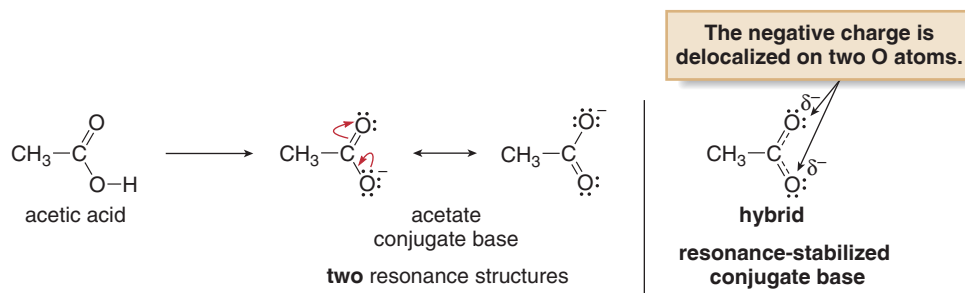
A third factor that determines acidity is resonance. Recall from Section 1.5 that resonance occurs whenever two or more different Lewis structures can be drawn for the same arrangement of atoms. To illustrate this phenomenon, compare ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and acetic acid (CH_3COOH), two different compounds containing O–H bonds. Based on Table 2.1, CH_3COOH is a stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$:



Draw the conjugate bases of these acids to illustrate the importance of resonance. For ethoxide ($\text{CH}_3\text{CH}_2\text{O}^-$), the conjugate base of ethanol, only one Lewis structure can be drawn. The negative charge of this conjugate base is *localized* on the O atom.



With acetate (CH_3COO^-), however, two resonance structures can be drawn.



Resonance delocalization often produces a larger effect on $\text{p}K_{\text{a}}$ than the inductive effects discussed in Section 2.5B. Resonance makes CH_3COOH ($\text{p}K_{\text{a}} = 4.8$) a much stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$ ($\text{p}K_{\text{a}} = 16$), while the inductive effects due to three electronegative F atoms make $\text{CF}_3\text{CH}_2\text{OH}$ ($\text{p}K_{\text{a}} = 12.4$) a somewhat stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$.

The difference in these two resonance structures is the **position of a π bond** and a **lone pair**. Although each resonance structure of acetate implies that the negative charge is localized on an O atom, in actuality, charge is **delocalized** over both O atoms. **Delocalization of electron density stabilizes acetate, making it a weaker base.**

Remember that neither resonance form adequately represents acetate. The true structure is a **hybrid** of both structures. In the hybrid, the electron pairs drawn in different locations in individual resonance structures are **delocalized**. With acetate, a dashed line is used to show that each C–O bond has partial double bond character. The symbol δ^- (partial negative) indicates that the charge is delocalized on both O atoms in the hybrid.

Thus, **resonance delocalization makes CH_3COO^- more stable than $\text{CH}_3\text{CH}_2\text{O}^-$, so CH_3COOH is a stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$.** This is another example of a general rule.

- The acidity of H--A increases when the conjugate base A^- is resonance stabilized.

Electrostatic potential plots of $\text{CH}_3\text{CH}_2\text{O}^-$ and CH_3COO^- in Figure 2.3 indicate that the negative charge is concentrated on a single O in $\text{CH}_3\text{CH}_2\text{O}^-$, but delocalized over the O atoms in CH_3COO^- .

Problem 2.21

The C–H bond in acetone, $(\text{CH}_3)_2\text{C}=\text{O}$, has a $\text{p}K_{\text{a}}$ of 19.2. Draw two resonance structures for its conjugate base. Then, explain why acetone is much more acidic than propane, $\text{CH}_3\text{CH}_2\text{CH}_3$ ($\text{p}K_{\text{a}} = 50$).

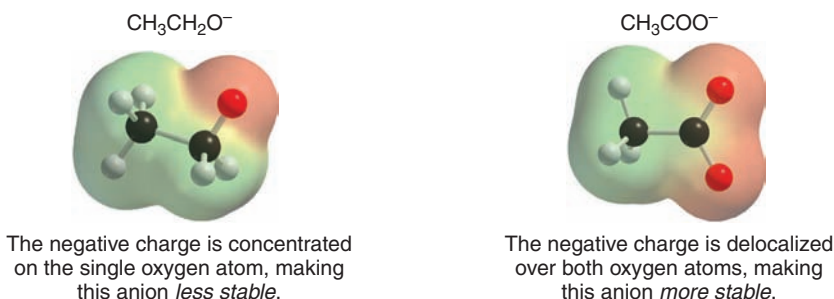
Problem 2.22

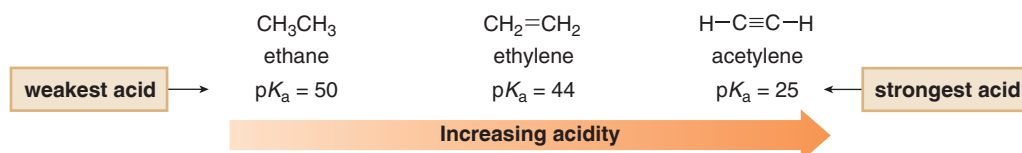
Acetonitrile (CH_3CN) has a $\text{p}K_{\text{a}}$ of 25, making it more acidic than many other compounds having only C–H bonds. Draw Lewis structures for acetonitrile and its conjugate base. Use resonance structures to account for the acidity of acetonitrile.

2.5D Hybridization Effects

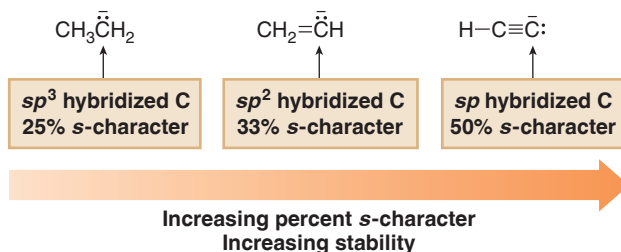
The final factor affecting the acidity of H--A is the hybridization of A. To illustrate this phenomenon, compare ethane (CH_3CH_3), ethylene ($\text{CH}_2=\text{CH}_2$), and acetylene ($\text{HC}\equiv\text{CH}$), three different compounds containing C–H bonds. Appendix A indicates that there is a considerable difference in the $\text{p}K_{\text{a}}$ values of these compounds.

Figure 2.3
Electrostatic potential plots of $\text{CH}_3\text{CH}_2\text{O}^-$ and CH_3COO^-





The conjugate bases formed by removing a proton from ethane, ethylene, and acetylene are each carbanions—**species with a negative charge on carbon**.



Note, however, that the hybridization of the carbon bearing the negative charge is different in each anion, so the lone pair of electrons occupies an orbital with a different percent *s*-character in each case. A higher percent *s*-character means a hybrid orbital has a larger fraction of the lower energy *s* orbital.

- The *higher* the percent *s*-character of the hybrid orbital, the **more stable** the conjugate base.

Thus, **acidity increases from CH_3CH_3 to $\text{CH}_2=\text{CH}_2$ to $\text{HC}\equiv\text{CH}$ as the negative charge of the conjugate base is stabilized by increasing percent *s*-character**. Once again this is a specific example of a general trend.

- The acidity of $\text{H}-\text{A}$ increases as the percent *s*-character of the A^- increases.

Electrostatic potential plots of these carbanions appear in Figure 2.4.

Problem 2.23

For each pair of compounds: [1] Which indicated H is more acidic? [2] Draw the conjugate base of each acid. [3] Which conjugate base is stronger?

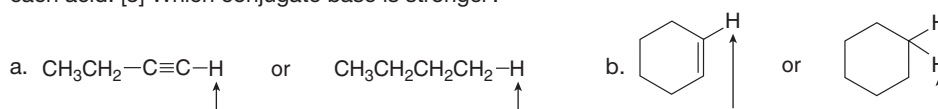
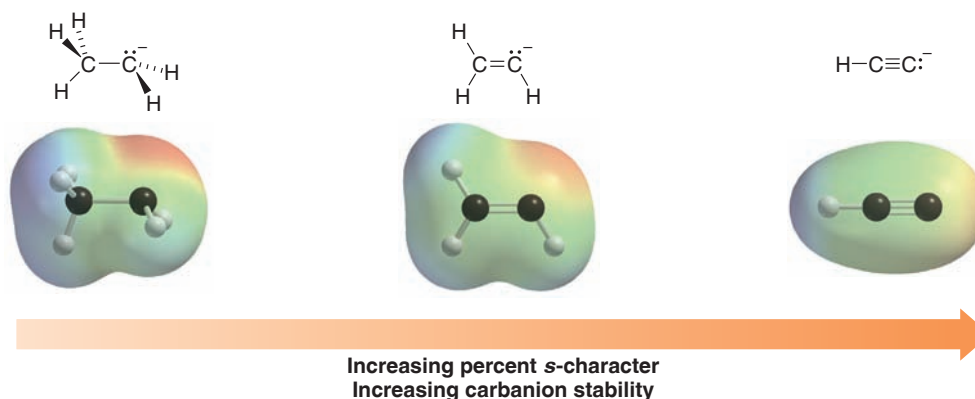


Figure 2.4
Electrostatic potential plots
of three carbanions



- As the lone pair of electrons is pulled closer to the nucleus, the negatively charged carbon appears less intensely red.

Figure 2.5

Summary of the factors that determine acidity

Factor	Example		
1. Element effects: The acidity of H–A increases both left-to-right across a row and down a column of the periodic table.			
2. Inductive effects: The acidity of H–A increases with the presence of electron-withdrawing groups in A.	$\text{CH}_3\text{CH}_2\text{O}-\text{H}$	$\text{CF}_3\text{CH}_2\text{O}-\text{H}$	more acidic
3. Resonance effects: The acidity of H–A increases when the conjugate base A^- is resonance stabilized.	$\text{CH}_3\text{CH}_2\text{O}-\text{H}$	$\text{CH}_3\text{COO}-\text{H}$	more acidic
4. Hybridization effects: The acidity of H–A increases as the percent s-character of A^- increases.	CH_3CH_3	$\text{CH}_2=\text{CH}_2$	$\text{H}-\text{C}\equiv\text{C}-\text{H}$

2.5E Summary of Factors Determining Acid Strength

The ability to recognize the most acidic site in a molecule will be important throughout the study of organic chemistry. All the factors that determine acidity are therefore summarized in Figure 2.5. The following two-step procedure shows how these four factors can be used to determine the relative acidity of protons.

HOW TO Determine the Relative Acidity of Protons

Step [1] Identify the atoms bonded to hydrogen, and use periodic trends to assign relative acidity.

- The most common H–A bonds in organic compounds are C–H, N–H, and O–H. Because acidity increases left-to-right across a row, the relative acidity of these bonds is C–H < N–H < O–H. Therefore, H atoms bonded to C atoms are usually *less acidic* than H atoms bonded to any heteroatom.

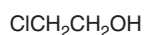
Step [2] If the two H atoms in question are bonded to the same element, draw the conjugate bases and look for other points of difference. Ask three questions:

- Do electron-withdrawing groups stabilize the conjugate base?
- Is the conjugate base resonance stabilized?
- How is the conjugate base hybridized?

Sample Problem 2.6 shows how to apply this procedure to actual compounds.

Sample Problem 2.6

Rank the following compounds in order of increasing acidity of their most acidic hydrogen atom.



A



B

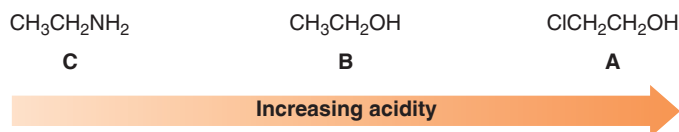


C

Solution

- [1] Compounds **A**, **B**, and **C** contain C–H, N–H, and O–H bonds. Because acidity increases left-to-right across a row of the periodic table, the O–H bonds are most acidic. Compound **C** is thus the least acidic because it has *no* O–H bonds.

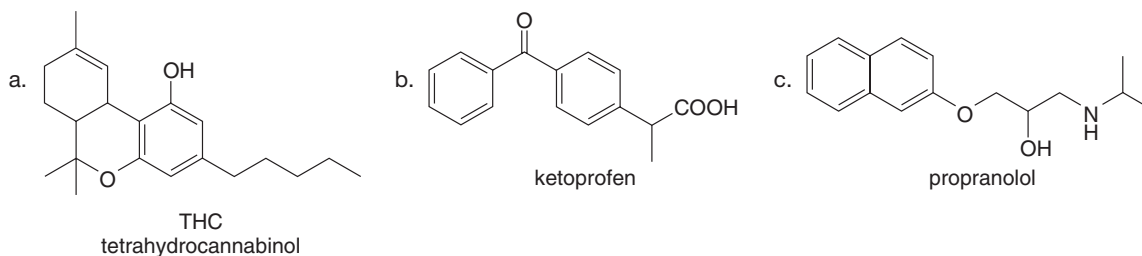
[2] The only difference between compounds **A** and **B** is the presence of an electronegative Cl in **A**. The Cl atom stabilizes the conjugate base of **A**, making it more acidic than **B**. Thus,



Problem 2.24 Rank the compounds in each group in order of increasing acidity.

- a. $\text{CH}_3\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{NH}_2$
- b. BrCH_2COOH , $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- c. $\text{CH}_3\text{CH}_2\text{NH}_2$, $(\text{CH}_3)_3\text{N}$, $\text{CH}_3\text{CH}_2\text{OH}$

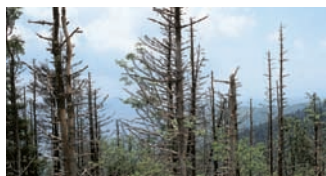
Problem 2.25 Which proton in each of the following drugs is most acidic? THC is the active component in marijuana, ketoprofen is an anti-inflammatory agent, and propranolol is an antihypertensive agent—that is, it lowers blood pressure.



2.6 Common Acids and Bases

Many strong or moderately strong acids and bases are used as reagents in organic reactions.

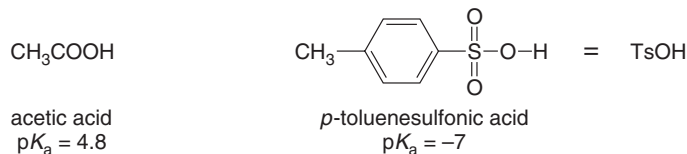
2.6A Common Acids



Sulfuric acid is the most widely produced industrial chemical. It is also formed when sulfur oxides, emitted into the atmosphere by burning fossil fuels high in sulfur content, dissolve in water. This makes rainwater acidic, forming acid rain.

Several organic reactions are carried out in the presence of strong inorganic acids, most commonly **HCl** and **H₂SO₄**. These strong acids, with **pK_a values ≤ 0**, should be familiar from previous chemistry courses.

Two organic acids are also commonly used, namely **acetic acid** and ***p*-toluenesulfonic acid** (usually abbreviated as **TsOH**). Although acetic acid has a higher pK_a than the inorganic acids, making it a weaker acid, it is more acidic than most organic compounds. *p*-Toluenesulfonic acid is similar in acidity to the strong inorganic acids. Because it is a solid, small quantities can be easily weighed on a balance and then added to a reaction mixture.



2.6B Common Bases

Common strong bases used in organic reactions are more varied in structure. Three common kinds of negatively charged bases include:

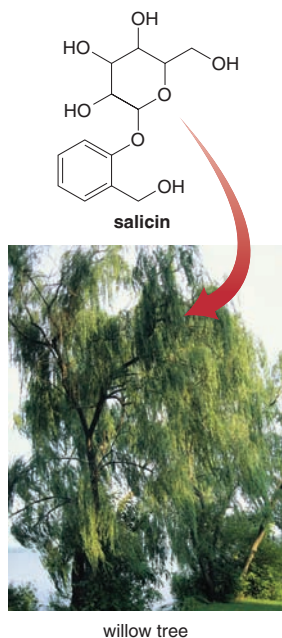
- [1] Negatively charged oxygen bases: **⁻OH** (hydroxide) and its organic derivatives
- [2] Negatively charged nitrogen bases: **⁻NH₂** (amide) and its organic derivatives
- [3] Hydride (**H⁻**)

Figure 2.6 gives examples of these strong bases. Each negatively charged base is used as a salt with a spectator ion (usually Li⁺, Na⁺, or K⁺) that serves to balance charge.

Figure 2.6

Some common negatively charged bases

The modern history of aspirin (Section 2.7) dates back to 1763 when Reverend Edmund Stone reported on the analgesic effect of chewing on the bark of the willow tree. Willow bark is now known to contain *salicin*, which is structurally related to aspirin.

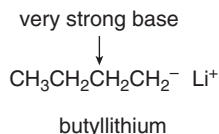


oxygen bases		nitrogen bases	
$\text{Na}^+ \text{ } ^-\text{OH}$	sodium hydroxide	$\text{Na}^+ \text{ } ^-\text{NH}_2$	sodium amide
$\text{Na}^+ \text{ } ^-\text{OCH}_3$	sodium methoxide	$\text{Li}^+ \text{ } ^-\text{N}[\text{CH}(\text{CH}_3)_2]_2$	lithium diisopropylamide
$\text{Na}^+ \text{ } ^-\text{OCH}_2\text{CH}_3$	sodium ethoxide		
$\text{K}^+ \text{ } ^-\text{OC}(\text{CH}_3)_3$	potassium <i>tert</i> -butoxide		
		hydride	
		$\text{Na}^+ \text{ } ^-\text{H}$	sodium hydride

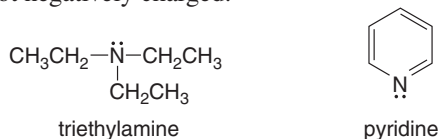
- Strong bases have weak conjugate acids with high $\text{p}K_{\text{a}}$ values, usually > 12 .

Strong bases have a net negative charge, but not all negatively charged species are strong bases. For example, none of the halides, F^- , Cl^- , Br^- , or I^- , is a strong base. These anions have very strong conjugate acids and have little affinity for donating their electron pairs to a proton.

Carbanions, negatively charged carbon atoms discussed in Section 2.5D, are especially strong bases. Perhaps the most common example is **butyllithium**. Butyllithium and related compounds are discussed in greater detail in Chapter 20.



Two other weaker organic bases are **triethylamine** and **pyridine**. These compounds have a lone pair on nitrogen, making them basic, but they are considerably weaker than the amide bases because they are neutral, not negatively charged.



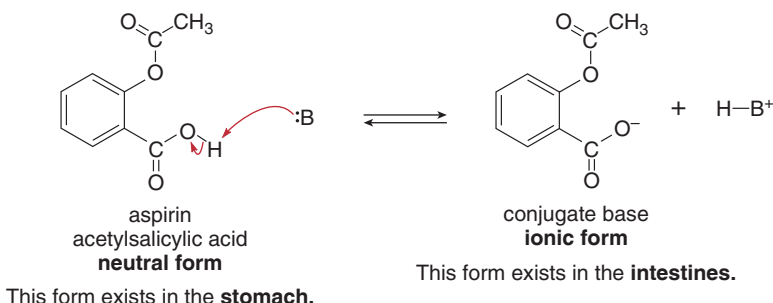
Problem 2.26

Draw the products formed when 2-propanol [$(\text{CH}_3)_2\text{CHOH}$], the main ingredient in rubbing alcohol, is treated with each acid or base: (a) NaH ; (b) H_2SO_4 ; (c) $\text{Li}^+ \text{ } ^-\text{N}[\text{CH}(\text{CH}_3)_2]_2$; (d) $\text{CH}_3\text{CO}_2\text{H}$.

2.7 Aspirin

Aspirin, or acetylsalicylic acid, is the most well known member of a group of compounds called **salicylates**. Although aspirin was first used in medicine for its analgesic (pain-relieving), anti-pyretic (fever-reducing), and anti-inflammatory properties, today it is commonly used as an anti-platelet agent in the treatment and prevention of heart attacks and strokes. **Aspirin is a synthetic compound**; it does not occur in nature, though some related salicylates are found in willow bark and meadowsweet blossoms.

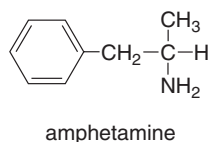
Like many drugs, aspirin is capable of undergoing a proton transfer reaction. Its most acidic proton is the H bonded to O, and in the presence of base, this H is readily removed.



Why is this acid–base reaction important? After ingestion, aspirin first travels into the stomach and then the intestines. In the acidic environment of the stomach, aspirin remains in its neutral form, but in the basic environment of the small intestine, aspirin is deprotonated to form its conjugate base, an ion.

Whether aspirin is present as its acid or its conjugate base is very important in determining whether it can permeate a cell. **To be active, aspirin must cross a cell membrane, and to do so, it must be neutral, not ionic.** This means that aspirin crosses a cell membrane and is absorbed by the body in its neutral form in the stomach. Aspirin's mechanism of action is discussed in greater detail in Chapter 19.

Problem 2.27



Compounds like amphetamine that contain nitrogen atoms are protonated by the HCl in the gastric juices of the stomach, and the resulting salt is then deprotonated in the basic environment of the intestines to regenerate the neutral form. Write proton transfer reactions for both of these processes. Where is amphetamine likely to be absorbed by the body?

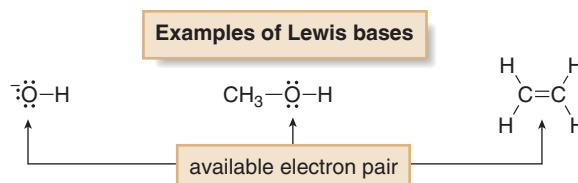
2.8 Lewis Acids and Bases

The Lewis definition of acids and bases is more general than the Brønsted–Lowry definition.

- A Lewis acid is an *electron pair acceptor*.
- A Lewis base is an *electron pair donor*.

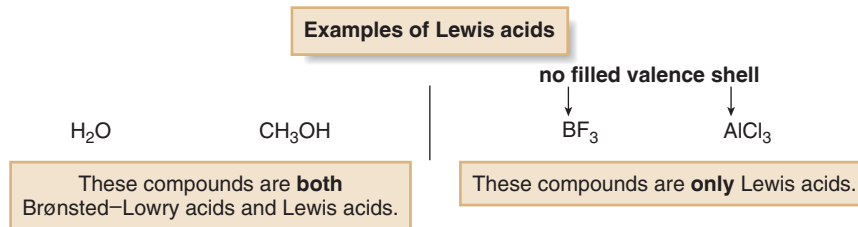
Lewis bases are structurally the same as Brønsted–Lowry bases. Both have an **available electron pair**—a lone pair or an electron pair in a π bond. A Brønsted–Lowry base always donates this electron pair to a proton, but a Lewis base donates this electron pair to anything that is electron deficient.

All Brønsted–Lowry bases are Lewis bases.



A Lewis acid must be able to accept an electron pair, but there are many ways for this to occur. **All Brønsted–Lowry acids are also Lewis acids, but the reverse is not necessarily true.** Any species that is electron deficient and capable of accepting an electron pair is also a Lewis acid.

Common examples of Lewis acids (which are not Brønsted–Lowry acids) include BF_3 and AlCl_3 . These compounds contain elements in group 3A of the periodic table that can accept an electron pair because they do not have filled valence shells of electrons.



Problem 2.28

Which compounds are Lewis bases?

- a. NH_3 b. $\text{CH}_3\text{CH}_2\text{CH}_3$ c. H^- d. $\text{H}-\text{C}\equiv\text{C}-\text{H}$

Problem 2.29

Which compounds are Lewis acids?

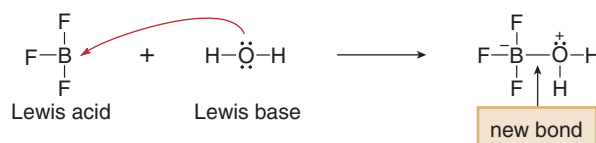
- a. BBr_3 b. $\text{CH}_3\text{CH}_2\text{OH}$ c. $(\text{CH}_3)_3\text{C}^+$ d. Br^-

Any reaction in which one species donates an electron pair to another species is a Lewis acid–base reaction.

In a Lewis acid–base reaction, a Lewis base donates an electron pair to a Lewis acid. Most of the reactions in organic chemistry involving movement of electron pairs can be classified as Lewis acid–base reactions. Lewis acid–base reactions illustrate a general pattern of reactivity in organic chemistry.

- Electron-rich species react with electron-poor species.

In the simplest Lewis acid–base reaction one bond is formed and no bonds are broken. This is illustrated with the reaction of BF_3 with H_2O . BF_3 has only six electrons around B, so it is the electron-deficient Lewis acid. H_2O has two lone pairs on O, so it is the electron-rich Lewis base.



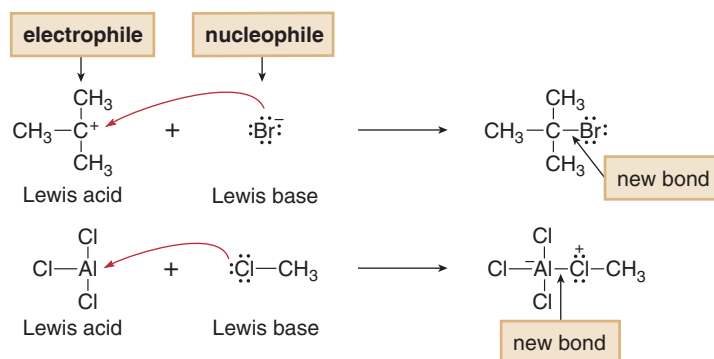
H_2O donates an electron pair to BF_3 to form one new bond. The electron pair in the new B–O bond comes from the oxygen atom, and a single product is formed. Both B and O bear formal charges in the product, but the overall product is neutral.

Nucleophile = nucleus loving.
Electrophile = electron loving.

- A Lewis acid is also called an *electrophile*.
- When a Lewis base reacts with an electrophile other than a proton, the Lewis base is also called a *nucleophile*.

In this Lewis acid–base reaction, **BF_3 is the electrophile** and **H_2O is the nucleophile**.

Two other examples are drawn. In each reaction the **electron pair is not removed from the Lewis base**; instead, the electron pair is donated to an atom of the Lewis acid, and one new covalent bond is formed.

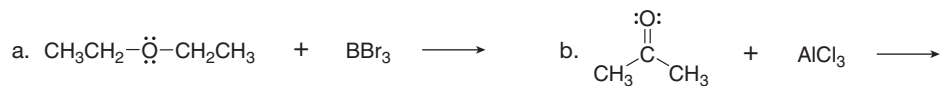


Problem 2.30

For each reaction, label the Lewis acid and base. Use curved arrow notation to show the movement of electron pairs.

- a. $\text{BF}_3 + \text{CH}_3\text{-}\ddot{\text{O}}\text{-CH}_3 \longrightarrow \text{F}_3\text{B-}\overset{+}{\text{O}}(\text{CH}_3)_2$
- b. $(\text{CH}_3)_2\text{CH}^+ + \text{OH}^- \longrightarrow (\text{CH}_3)_2\text{CHOH}$

Problem 2.31 Draw the products of each reaction, and label the nucleophile and electrophile.

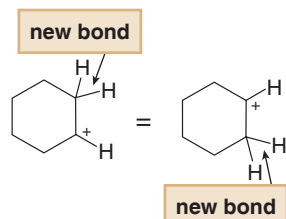


Problem 2.32 Draw the product formed when $(\text{CH}_3\text{CH}_2)_3\text{N:}$, a Lewis base, reacts with each Lewis acid: (a) $\text{B}(\text{CH}_3)_3$; (b) $(\text{CH}_3)_3\text{C}^+$; (c) AlCl_3 .

In some Lewis acid–base reactions, one bond is formed and one bond is broken. To draw the products of these reactions, keep the following steps in mind.

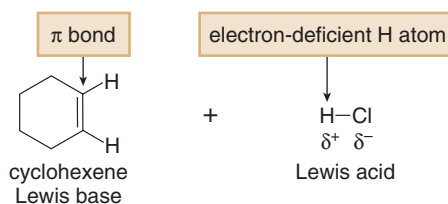
- [1] Always identify the Lewis acid and base first.
- [2] Draw a curved arrow from the electron pair of the base to the electron-deficient atom of the acid.
- [3] Count electron pairs and break a bond when needed to keep the correct number of valence electrons.

Recall from Chapter 1 that a positively charged carbon atom is called a **carbocation**.

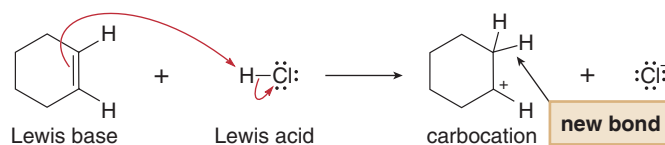


In the reaction of cyclohexene with HCl, the new bond to H could form at **either carbon of the double bond**, because the same carbocation results.

For example, draw the Lewis acid–base reaction between cyclohexene and $\text{H}-\text{Cl}$. The Brønsted–Lowry acid HCl is also a Lewis acid, and cyclohexene, having a π bond, is the Lewis base.



To draw the product of this reaction, the electron pair in the π bond of the Lewis base forms a new bond to the proton of the Lewis acid, forming a carbocation. The $\text{H}-\text{Cl}$ bond must break, giving its two electrons to Cl, forming Cl^- . Because two electron pairs are involved, two curved arrows are needed.



The Lewis acid–base reaction of cyclohexene with HCl is a specific example of a fundamental reaction of compounds containing $\text{C}-\text{C}$ double bonds, as discussed in Chapter 10.

Problem 2.33 Label the Lewis acid and base. Use curved arrow notation to show the movement of electron pairs.



KEY CONCEPTS

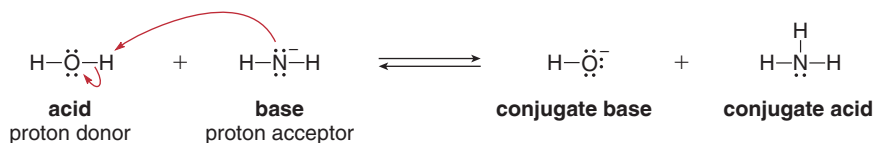
Acids and Bases

A Comparison of Brønsted–Lowry and Lewis Acids and Bases

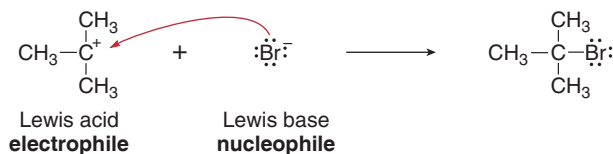
Type	Definition	Structural feature	Examples
Brønsted–Lowry acid (2.1)	proton donor	a proton	HCl , H_2SO_4 , H_2O , CH_3COOH , TsOH
Brønsted–Lowry base (2.1)	proton acceptor	a lone pair or a π bond	OH^- , OCH_3^- , H^- , NH_2^- , NH_3 , $\text{CH}_2=\text{CH}_2$
Lewis acid (2.8)	electron pair acceptor	a proton, or an unfilled valence shell, or a partial (+) charge	BF_3 , AlCl_3 , HCl , CH_3COOH , H_2O
Lewis base (2.8)	electron pair donor	a lone pair or a π bond	OH^- , OCH_3^- , H^- , NH_2^- , NH_3 , $\text{CH}_2=\text{CH}_2$

Acid–Base Reactions

[1] A Brønsted–Lowry acid donates a proton to a Brønsted–Lowry base (2.2).



[2] A Lewis base donates an electron pair to a Lewis acid (2.8).

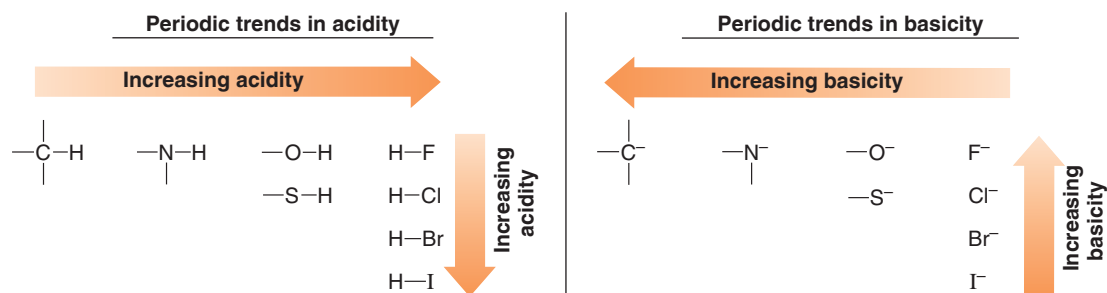


- Electron-rich species react with electron-poor ones.
- Nucleophiles react with electrophiles.

Important Facts

- Definition: $\text{p}K_{\text{a}} = -\log K_{\text{a}}$. The lower the $\text{p}K_{\text{a}}$, the stronger the acid (2.3).
- The stronger the acid, the weaker the conjugate base (2.3).
- In proton transfer reactions, equilibrium favors the weaker acid and weaker base (2.4).
- An acid can be deprotonated by the conjugate base of any acid having a higher $\text{p}K_{\text{a}}$ (2.4).

Periodic Trends in Acidity and Basicity (2.5A)



Factors That Determine Acidity (2.5)

- | | |
|---|---|
| [1] Element effects (2.5A) | The acidity of H–A increases both left-to-right across a row and down a column of the periodic table. |
| [2] Inductive effects (2.5B) | The acidity of H–A increases with the presence of electron-withdrawing groups in A. |
| [3] Resonance effects (2.5C) | The acidity of H–A increases when the conjugate base A^- is resonance stabilized. |
| [4] Hybridization effects (2.5D) | The acidity of H–A increases as the percent s-character of the A^- increases. |

PROBLEMS

Brønsted–Lowry Acids and Bases

2.34 What is the conjugate acid of each base?

- a. H_2O b. NH_2^- c. HCO_3^- d. $\text{CH}_3\text{CH}_2\text{NHCH}_3$ e. CH_3OCH_3 f. CH_3COO^-

2.35 What is the conjugate base of each acid?

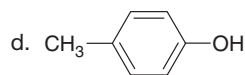
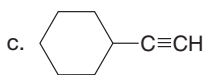
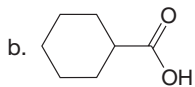
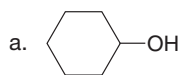
- a. HCN b. HCO_3^- c. $(\text{CH}_3)_2\text{NH}_2^+$ d. $\text{HC}\equiv\text{CH}$ e. $\text{CH}_3\text{CH}_2\text{COOH}$ f. $\text{CH}_3\text{SO}_3\text{H}$

Reactions of Brønsted–Lowry Acids and Bases

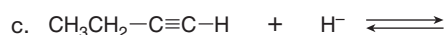
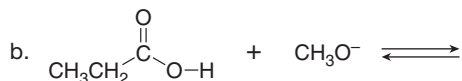
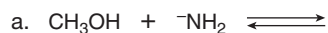
2.36 Draw the products formed from the acid–base reaction of H_2SO_4 with each compound.

- a. b. c. d.

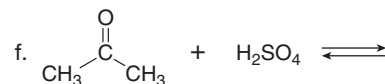
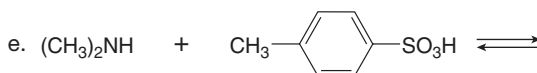
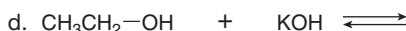
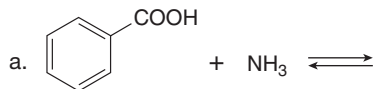
2.37 Draw the products formed from the acid–base reaction of KOH with each compound.



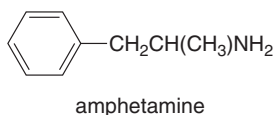
2.38 Draw the products of each proton transfer reaction. Label the acid and base in the starting materials, and the conjugate acid and base in the products.



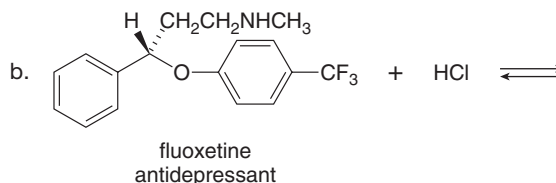
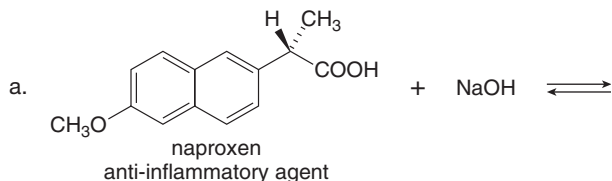
2.39 Draw the products of each acid–base reaction.



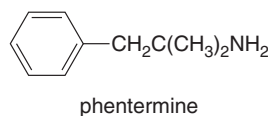
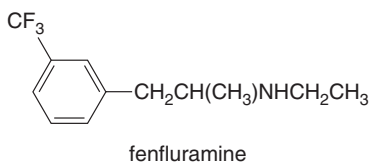
2.40 Amphetamine is a powerful stimulant of the central nervous system. Draw the products formed from the acid–base reaction of amphetamine with each reagent: (a) HCl; (b) NaH.



2.41 Draw the products of each acid–base reaction.

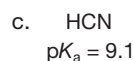
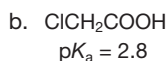
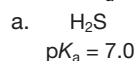


2.42 Fenfluramine and phentermine are two components of fen–phen, an appetite suppressant withdrawn from the market in 1997 after it was shown to damage the heart valves in some patients. What products are formed when fenfluramine and phentermine are each treated with acetic acid ($\text{CH}_3\text{CO}_2\text{H}$)?

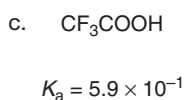
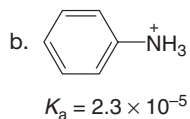
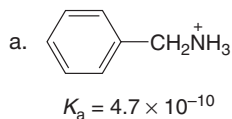


pK_a , K_a , and the Direction of Equilibrium

2.43 What is K_a for each compound? Use a calculator when necessary.

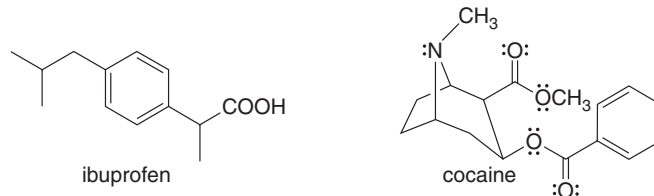


2.44 What is the pK_a for each compound? Use a calculator when necessary.



2.55 Many drugs are Brønsted–Lowry acids or bases.

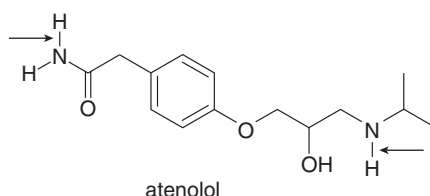
- What is the most acidic proton in the analgesic ibuprofen? Draw the conjugate base.
- What is the most basic electron pair in cocaine? Draw the conjugate acid.



2.56 The pK_a of nitromethane (CH_3NO_2) is 10, making its C–H bond more acidic than most C–H bonds. Explain.

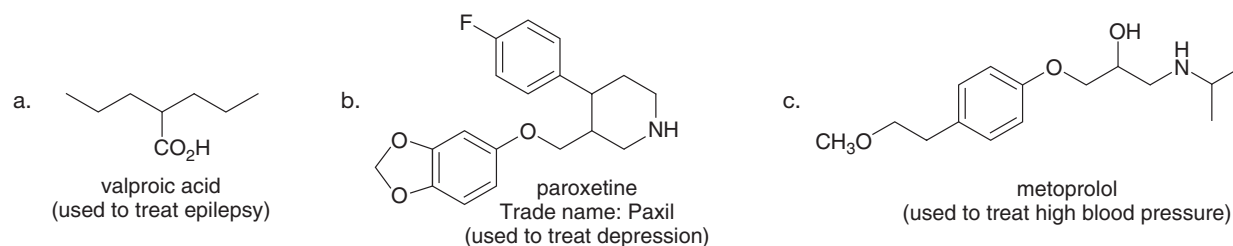
2.57 Dimethyl ether (CH_3OCH_3) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) are isomers, but CH_3OCH_3 has a pK_a of 40 and $\text{CH}_3\text{CH}_2\text{OH}$ has a pK_a of 16. Why are these pK_a values so different?

2.58 Atenolol is a β (beta) blocker, a drug used to treat high blood pressure. Which of the indicated N–H bonds is more acidic? Explain your reasoning.



2.59 Ethyl butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$, is one of the many organic compounds isolated from mangoes. Which hydrogen is most readily removed when ethyl butanoate is treated with base? Propose a reason for your choice, and using the data in Appendix A, estimate its pK_a .

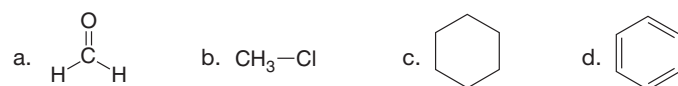
2.60 Use the principles in Section 2.5 to label the most acidic hydrogen in each drug. Explain your choice.



2.61 Label the three most acidic hydrogen atoms in lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, and rank them in order of decreasing acidity. Explain your reasoning.

Lewis Acids and Bases

2.62 Classify each compound as a Lewis base, a Brønsted–Lowry base, both, or neither.

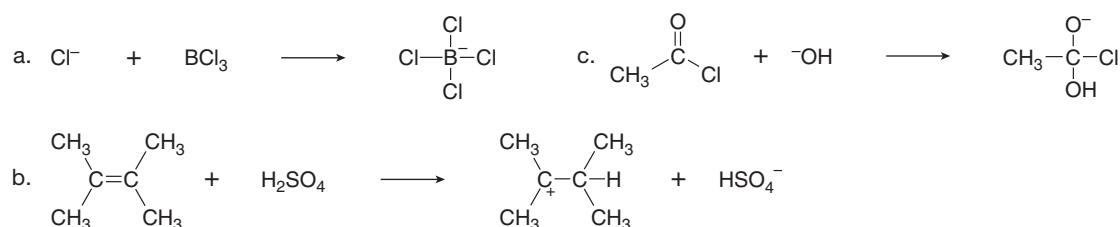


2.63 Classify each species as a Lewis acid, a Brønsted–Lowry acid, both, or neither.

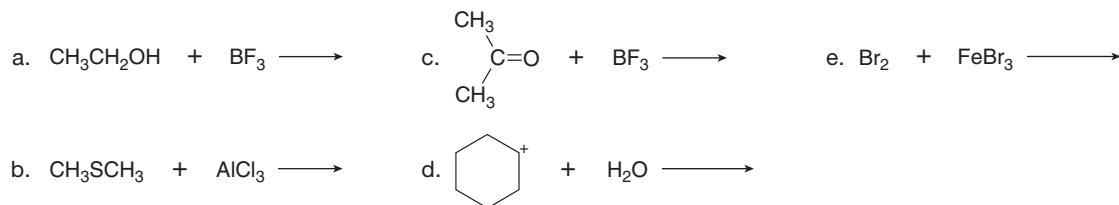


Lewis Acid–Base Reactions

2.64 Label the Lewis acid and Lewis base in each reaction. Use curved arrows to show the movement of electron pairs.



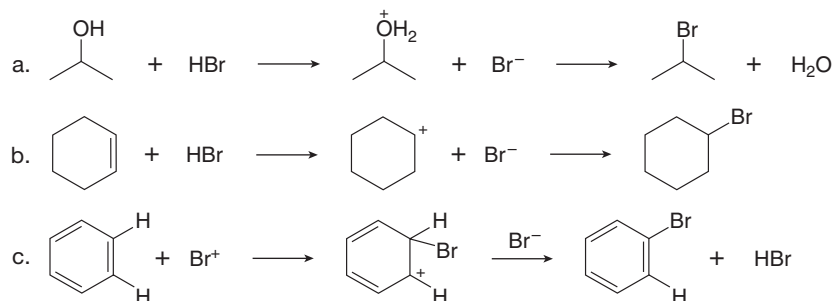
2.65 Draw the products of each Lewis acid–base reaction. Label the electrophile and nucleophile.



2.66 Draw the product formed when the Lewis acid $(\text{CH}_3\text{CH}_2)_3\text{C}^+$ reacts with each Lewis base: (a) H_2O ; (b) CH_3OH ; (c) $(\text{CH}_3)_2\text{O}$; (d) NH_3 ; (e) $(\text{CH}_3)_2\text{NH}$.

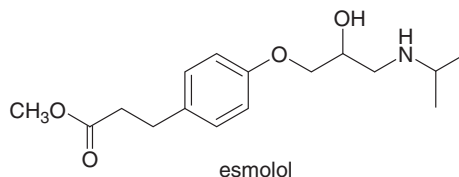
General

2.67 Classify each reaction as either a proton transfer reaction, or a reaction of a nucleophile with an electrophile. Use curved arrows to show how the electron pairs move.



2.68 Hydroxide (^-OH) can react as a Brønsted–Lowry base (and remove a proton), or a Lewis base (and attack a carbon atom). (a) What organic product is formed when ^-OH reacts with the carbocation $(\text{CH}_3)_3\text{C}^+$ as a Brønsted–Lowry base? (b) What organic product is formed when ^-OH reacts with $(\text{CH}_3)_3\text{C}^+$ as a Lewis base?

2.69 Answer the following questions about esmolol, a drug used to treat high blood pressure sold under the trade name Brevibloc.



- Label the two most acidic hydrogen atoms in esmolol, and explain which H is more acidic.
- What products are formed when esmolol is treated with NaH ?
- What products are formed when esmolol is treated with HCl ?
- Label all sp^2 hybridized C atoms.
- Label the only trigonal pyramidal atom.
- Label all C's that bear a δ^+ charge.

Challenge Problems

2.70 Molecules like acetamide (CH_3CONH_2) can be protonated on either their O or N atoms when treated with a strong acid like HCl . Which site is more readily protonated and why?

2.71 Two pK_a values are reported for malonic acid, a compound with two COOH groups. Explain why one pK_a is lower and one pK_a is higher than the pK_a of acetic acid (CH_3COOH , $pK_a = 4.8$).

