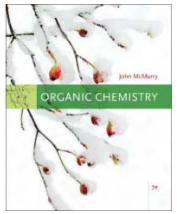
Organic Chemistry (1)

Spring 2013

Professors: Yuguo Ma （马玉国）
Dahui Zhao （赵达慧）

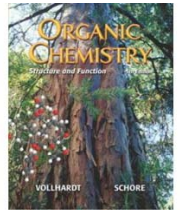
Organic Chemistry

Class Schedule: **Wednesday 8:00 AM - 9:50 AM**
Friday 10:10 AM - 12:00 PM



Textbooks: John E. McMurry, *Organic Chemistry*, 7th Ed., 2008
Vollhardt; Schore, *Organic Chemistry*, 5th Ed., 2007

50 copies total available at: 化学楼 B437



基础有机化学（第三版）邢其毅 裴伟伟等著 (optional)

Lecture Notes & Course FTP:

ftp://dhzhao:engorg@ftp.chem.pku.edu.cn

Syllabus

Part I. Introduction (lecture 1)

Part II. Alkanes and cycloalkanes (lectures 2-4)

Part III. Stereochemistry (lectures 5-6)

Part IV. Alkyl Halides: Substitution and Elimination Reactions (lectures 6-8)

Part V. Organometallic Compounds (lecture 8)

Part VI. Alkenes (lectures 9-12)

Part VII. Alkynes (lecture 13)

Part VIII. Identification of Organic Compounds (lectures 14-15)

Mid-term Exam

Syllabus

Part IX. Alcohol and Ether (lectures 16-17)

Part X. Aromatic Compounds (lectures 18-20)

Part XI. Carbonyl Compounds: Aldehydes and Ketones (lectures 21-22)

Part XII. Carbonyl Compounds: Carboxylic Acids (lectures 23-24)

Part XIII. Carboxylic Acid Derivatives: Nucleophilic Acyl Substitution Reactions (lectures 25-26)

Part XIV. Carbonyl Condensation Reactions (lectures 27-28)

Review Sessions (2 lectures)

Final Exam

Grading

Grading: (100 Points)

Assignments:	2 assignments (2 points each)
Quizzes:	4-5 quizzes (2-3 points each)
Midterm Exam:	25 points
Final Exam:	60 points

Assignments/quizzes:

A number of assignments and quizzes will be given during the semester; each assignment/quiz is 2-3 points, totally worth 15 points toward your final grade; quizzes will be announced at least 3 days before they take place.

Exams: Midterm exam: week 8 or 9 (exact date to be announced)
Final exam: **8:30-10:30 AM, June 21, 2013**

Help and Resources

- Office hours（答疑）： Wednesday 2:00-4:30 PM

  Prof. Zhao : B437, Chemistry Building

  Prof. Ma : B419, Chemistry Building

  Email: dhzhao@pku.edu.cn, ygma@pku.edu.cn

  (individual appointments can be made through emails)

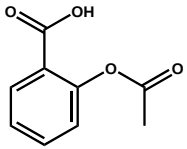
- Review sessions (before exams)

Remember, you cannot cram for an organic exam.
Organic chemistry is best learned by engaging the material everyday and in parts. Waiting until the last minute to study will leave an overwhelming amount of material to be learned in too little time. Consistency and discipline are the keys to success.

Organic Chemistry in Everyday Life: the Story of Aspirin

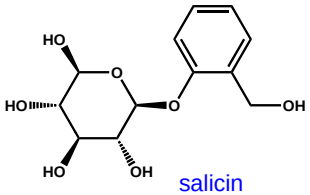
painkiller; reduces inflammation and cools fevers; helps with heart complaints

Aspirin



acetyl salicylic acid

400 BC: the Greek physician Hippocrates;
from willow leaves and barks

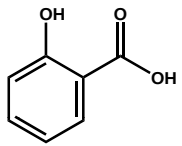


salicin

1897: Felix Hoffmann

irritant to the mouth and stomach

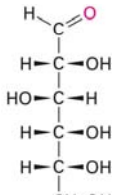
1763: Edward Stone



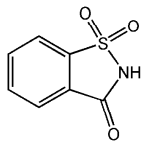
salicylic acid

Organic Chemistry in Everyday Life

Saccharin and aspartame: two popular sweeteners

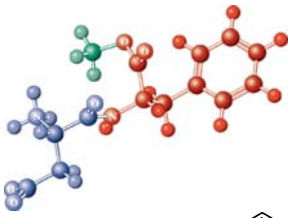


glucose

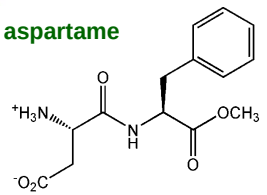


Saccharin

300 times as sweet as sugar, not metabolized, maybe carcinogenic



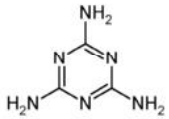
aspartame



200 times as sweet as sugar and contains 4 cal/g calorie

Melamine-Contaminated Milk Powder

Melamine (三聚氰胺)



N % of proteins: ~16% (average)

N % of melamine: 67%

Kjeldahl method for determining nitrogen: an internationally-recognized method for estimating the protein content in foods.

$$\text{Protein} + H_2SO_4 \longrightarrow CO_2 + (NH_4)_2SO_4 + SO_2$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O + 2NH_3$$

$$NH_3 + H_3BO_3 \longrightarrow NH_4H_2BO_3 + H_2O$$

pH Values of Household Products

Hair is composed of protein molecules, with disulfide bonds between polymer chains. Human hair strands are strongest at pH of 4-5 (disulfide bonds break at pH of 8-9, which causes cuticle roughness and split ends).

Shampoos are slightly basic (typically pH 8-9) to help remove the oils that hold dirt (drain cleaners at pH >11 can open clogged drains by partially dissolving hair).

Conditioners help restore pH balance to hair.

Pheromones of Insects

Pheromones (信息素): chemical messengers (outside the body)

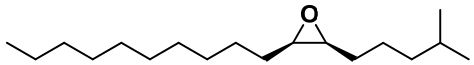
Greek word *pherein* (to transport) and *hormone* (impetus)

Insects can sense pheromones ~ 10^{-12} μg/mL

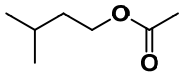
Types: aggregation, territorial, information, alarm, trail, sex…

Application:
pest trap/control (nontoxic and low concentration)

Gypsy moth pheromones



Alarm pheromone of honeybee



Introduction

Reading Materials: John E. McMurry: Chapters 1 and 2
Vollhardt; Schore: Chapter 1 and Section 2-2

You only have to read one of the two English books!

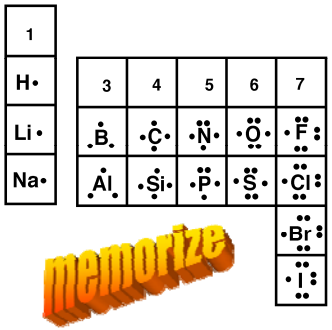
邢其毅 裴伟伟等: 第一、二章

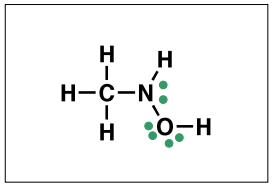
IUPAC nomenclature（命名法）will be introduced and used in our course; for Chinese nomenclature, please read Chapter 2 of the 邢 book.

Nomenclatures of different compounds and functionalities（官能团）will be introduced in each individual lecture/chapter in this course.

Important Concepts: ionic bond *vs*. covalent bond; σ bond and π bond; node; hybrid orbitals; molecular orbital (MO); bonding orbital & antibonding orbital; Lewis structure; octet rule; formal charge; resonance form; Brønsted-Lowry acid/base *vs*. Lewis acid/base.

Counting Valence Electrons





Count the available valence electrons

CH_5NO

5H x 1 = 5

1C x 4 = 4

1N x 5 = 5

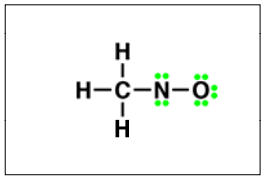
1O x 6 = 6

Valence e⁻⇨ 20

satisfying the octet rule

Lewis Structures - More Examples

Draw the Lewis Structure for CH_3NO



The trial structure has 20 valence electrons

We need to remove electrons but still satisfy the octet rule

Valence e⁻s?

CH_3NO

3H x 1 = 3

1C x 4 = 4

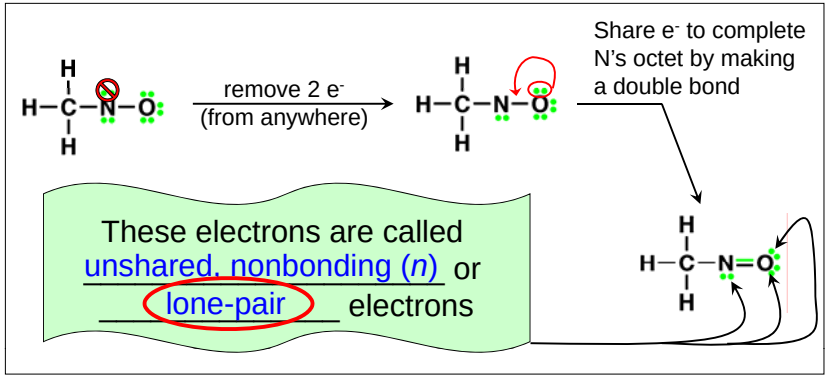
1N x 5 = 5

1O x 6 = 6

Valence e⁻⇨18

Electron Sharing

The trial structure is reconciled by removing the necessary number of electrons and adding multiple bonds

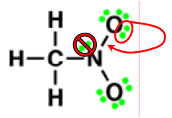


Lewis Structures

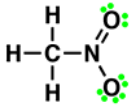
Try another example: CH_3NO_2

The atoms of CH_3NO_2 contribute 24 valence electrons

Trial structure



remove 2 e⁻ and share



Valence electrons

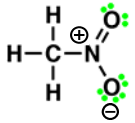
26

Charge in Lewis Structures

In the Lewis structure of CH_3NO_2 some atoms bear "extra" electrons while others are electron deficient. The notation of formal charge is used to express the surplus and shortage of electrons localized on individual atoms.

For any atom in a valid Lewis structure
Formal charge =

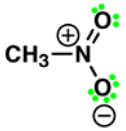
number valence electrons
(-) number nonbonded electrons
(-) 1/2 [number bonded electrons]



Verify this for yourself

Net Charge (Ionic Charge)

The net charge on the molecule is the sum of all formal charges



CH_3NO_2 has a net charge of zero
(it is a neutral molecule)

Molecules With Net Charge

Example: CO_3^{2-} carbonate anion

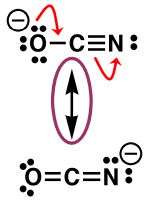
Counting valence electrons for charged molecules:
- add one electron for each negative charge
- take away one electron for each positive charge

Trial structure

26 e⁻

1C x 4 = 4
3O x 6 = 18
2e⁻ x 1 = 2
Valence e⁻⇨24

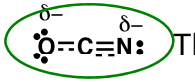
Delocalization and Resonance



The delocalization of electrons allows us to write alternative, valid Lewis structures

We draw more than one Lewis structure for the cyanate ion because the electrons are delocalized.

The two electron configurations are resonance structures.
(resonance contributors, resonance forms)

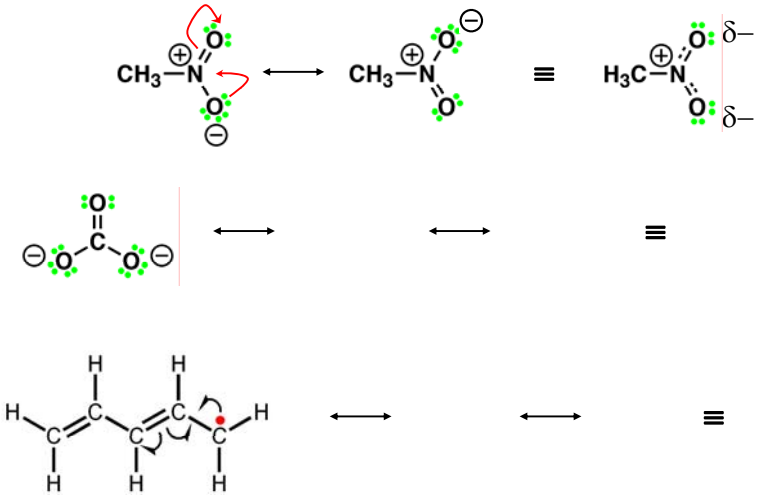


The actual structure is a resonance hybrid.

Delocalized form

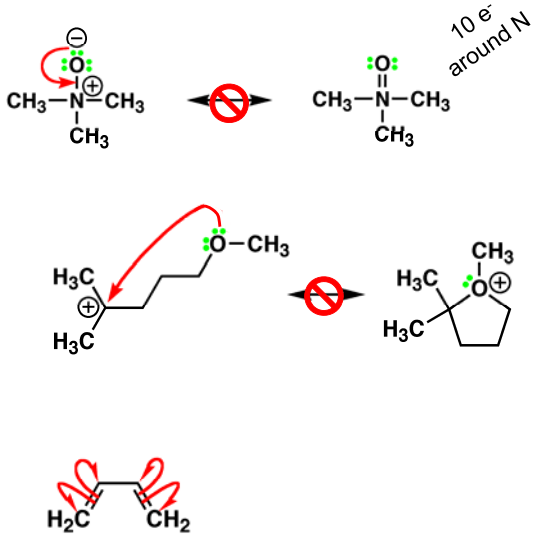
A special arrow convention is used to denote electronic configurations related as resonance contributors: ⟷.

More Examples of Electron Delocalization



Rules for Resonance Forms

1. **All resonance forms must obey normal rules of valency;**
2. **Resonance forms only differ in the place of their π or nonbonding electrons; the connectivity and position of the atoms do not change;**
3. **The number of unpaired electrons must remain the same.**

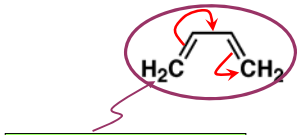


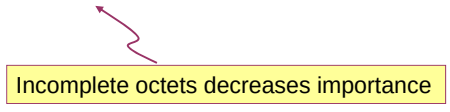
Resonance Forms

- **Individual resonance forms are imaginary, not real; the real structure is a resonance hybrid of the different forms;**
- **The resonance hybrid is more stable than any individual resonance form;**
- **Not all resonance forms are equivalent; the most important one is the major resonance contributor.**

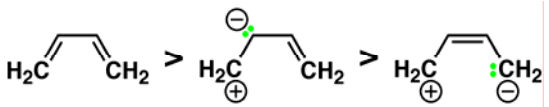
Guidelines for Determining the Importance of Resonance Forms

- **Structures with a maximum of octets and no charges are most important;**



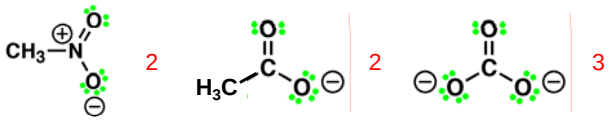


- **Structures with less separation of opposite charges are more important contributors; the further away two opposite charges are separated from each other, the less importance of the structure**

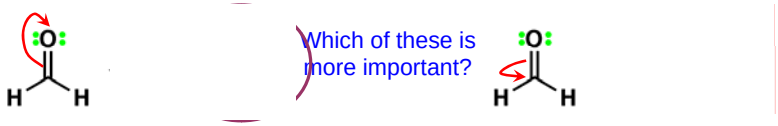


Relative Importance of Resonance Contributors

- **Systems having two or more equivalent resonance forms are more stable; the more resonance forms, the more stable**

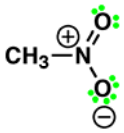
Stable  2 2 3

- **Negative charge should be preferentially located on the most electro-negative atom and positive charge on the least electronegative one;**



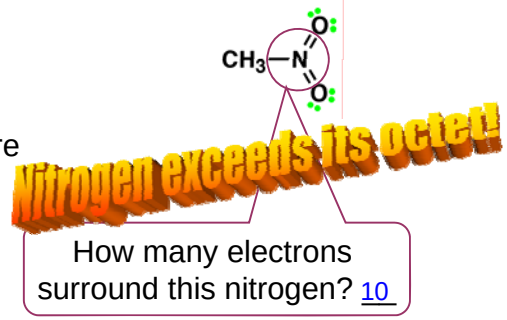
O is more electronegative than C

Common Mistakes



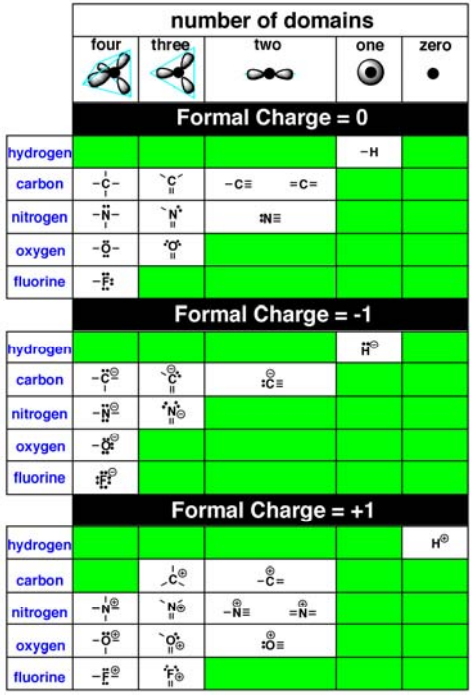
A valid Lewis structure

What's wrong with this structure?

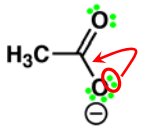


How many electrons surround this nitrogen? 10

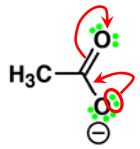
The Building Blocks of Organic Chemistry



Mistakes to Avoid for Proper Lewis Structures

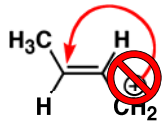
Incorrect 

What's wrong? 10 e⁻ around carbon

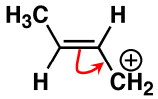
Correct 

Mistakes to Avoid Push electrons, not positive charges

Incorrect

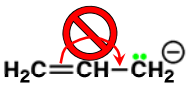


Correct

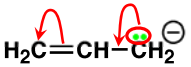


Mistakes to Avoid: Push electrons away from negative charge

Incorrect



Correct



Exceptions to the Octet Rule

Exception # 1 - not enough valence electrons

$CH_3\bullet$
methyl radical

$CH_3^{\oplus}$
methyl cation

NO
nitrogen oxide

Exception # 2 - early second row elements (Be, B)

BeH_2
beryllium hydride

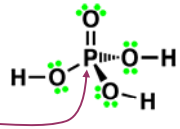
H–Be–H

BH_3
borane

Exceptions to the Octet Rule

Exception # 3 - beyond the second row, elements can be surrounded by more than eight electrons (valence shell expansion)

H_3PO_4
phosphoric acid



surrounded by 10 electrons

Under no circumstances can the second row elements be surrounded by more than eight electrons:

B, C, N, O, F

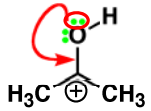
Practical Guidelines for Generating Resonance Contributors

Identify the "pushable" electrons (source)
- unshared electron pairs (atom w/ neutral or negative charge)
- pi electrons of multiple bonds

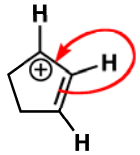
Identify the places to which electrons can be pushed i.e., the sink
- Atoms with formal positive charge
- Atoms that can accommodate formal negative charge

Identify a pathway of delocalized electrons that connects the pushable electrons to their destination

Generating Resonance Structures -Examples

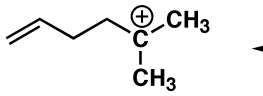


Source: lone pair
Sink: cation

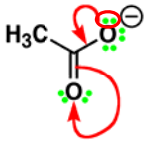


Source: π electrons
Sink: cation

Generating Resonance Structures - Examples



What's wrong?
No pathway of delocalized electrons



Source: lone pair (–)
Sink: electronegative atom