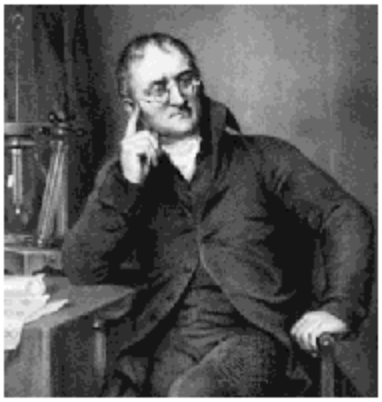
Chem 220 - Organic Chemistry

Problem Set 1 - Solution Set

Chapters 1 and 2, Structure, Bonding, Reactivity

Due: Monday, September 14, 2009



John Dalton

(1766-1844)

John Dalton's formulation of an Atomic Theory in the first decade of the 19th century provided a theoretical basis for understanding chemical behavior. In addition to defining the Law of Multiple Proportions, he also formulated the Rule of Greatest Simplicity, which held that water was a binary compound, OH. (Note: Dalton did not use our modern symbols, which came to us from Berzelius, but rather circles that were distinguishable from one another.) Dalton established the combining masses of H to O in water as ~1:6. This ratio was later refined to 1:8. Dalton postulated that in a molecules comprised of two different atoms, the simplest one in the series would be binary. While this rule applied to CO and CO_2, it did not apply to the pair, water and hydrogen peroxide. Thus, water, according to Dalton, was OH. The Rule of Greatest Simplicity, which was at odds with Gay-Lussac's Law of Combining Volumes of Gases, which demonstrated that the volume of hydrogen produced upon electrolysis of water was twice that of oxygen, was dismissed by Dalton as a faulty result. Moreover, although there was agreement regarding the combining masses of atoms in the first half of the nineteenth century, there was disagreement as to the unit mass of the common atoms encountered in organic chemistry: hydrogen (1), carbon (2x6 or 1x12), oxygen (2x8 or 1x16). Since hydrogen was the lightest of the elements, it was assigned a mass of one (Prout's Hypothesis), a notion that is unrelated to today's mass of hydrogen owing to the presence of a single proton in the hydrogen nucleus. Berzelius's proposal of a mass scale based upon O = 100 would have worked as well.

For a Brief History of Organic Chemistry (PowerPoint), click here.

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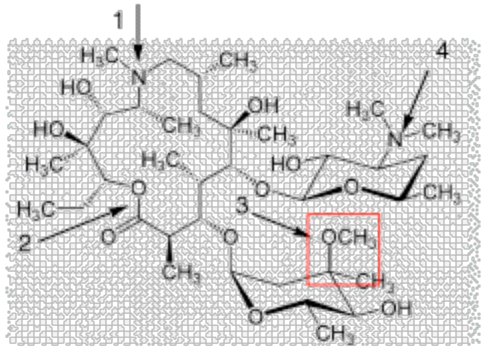
1. a) Identify the four functional groups in azithromycin marked by arrows. *1 and 4 are amines (amino group). 3 is an ether. 2 is an ester (carbalkoxy group; when an ester is part of a ring, it is called a lactone.) See the front, inside cover of Wade and Chapter 2*

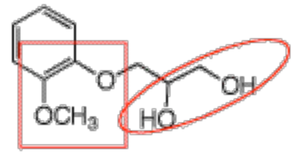
b) How many carboxyl groups are present in the four structures? Circle them. *See the circled groups below.*

c) Ethers (squares in structures below) can be of three types: dialkyl, alkyl-aryl (aromatic) or diaryl. Locate at least one of each type of ether amongst the four structures. ***Dialkyl ethers:*** *#3 in azithromycin. (Note: There are two six-membered rings in azithromycin that bear what looks like a cyclic ether. Because there is an oxygen attached to one of the carbons adjacent to the ring oxygen, the reactivity of these "ethers" is very different from normal ethers. These groups are acetals. Alkyl-aryl ethers: There are two in guaifenesin.* ***Diaryl ethers:*** *thyroxine.*

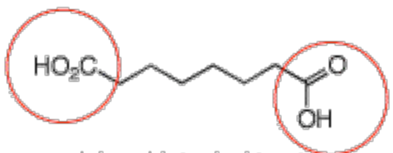
d) What is the structural difference between an alcohol and a phenol? Locate these groups in guaifenesin and thyroxine. *In alcohols, the -OH group is attached to an alkyl carbon. In phenols, it is attached to an aromatic (phenyl) ring. Alcohols have pKa's in the range of 16-18. Phenol itself has a pKa=10. Phenols are more acidic than alcohols.*



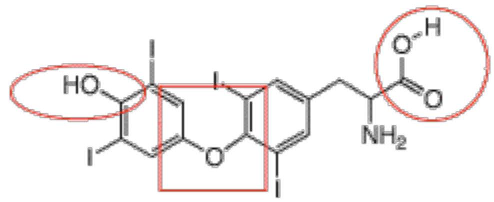
Azithromycin - semi-synthetic antibiotic



Guaifenesin - expectorant (Mucinex)



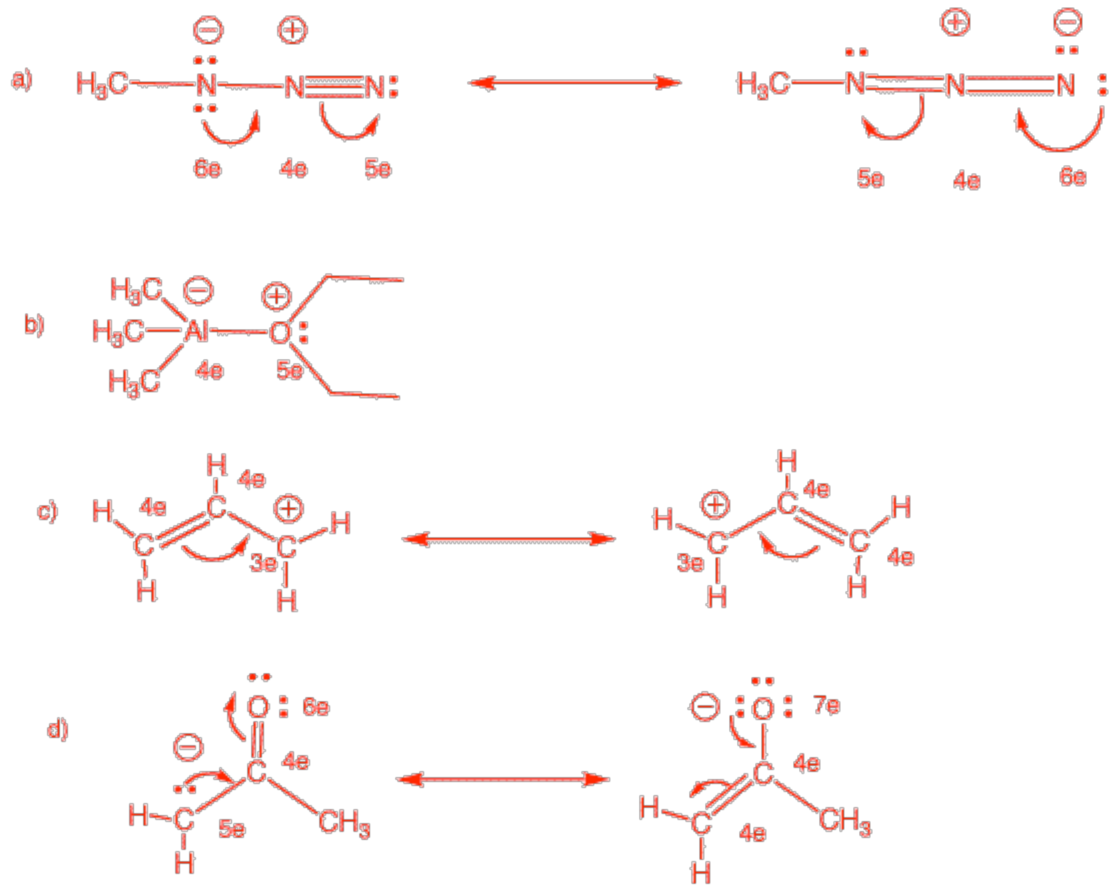
azelaic acid -topical treatment for rosacea (Finacia)



Thyroxine - thyroid hormone T4

2. Draw resonance structures (if they exist) for the following compounds. Include all formal charges. *Structures a), c) and d) have resonance structures. Charge, neutral, positive or negative is delocalized over several atoms. the electron count at each atom is provided (1/2 the electrons in each bond + the number of unpaired electrons. This count is compared to the neutral atom). In b), diethyl ether, a Lewis base, donates a pair of electrons to trimethylaluminum, a Lewis acid.*

a) CH_3N_3 b) $(CH_3)_3AlO(C_2H_5)_2$ c) $CH_2CHCH_2^+$ d) $^-CH_2COCH_3$



3. For each of the following acids or bases, identify the corresponding conjugate base or acid, whichever is appropriate. The pKa table may be of help.

a) $LiNH_2$ *conjugate acid is ammonia (NH_3)*

b) acetic acid *conjugate base is acetate ($CH_3CO_2^-$)*

c) $KOCH_3$ *conjugate acid is methanol (CH_3OH)*

d) CH_3CH_2MgBr *conjugate acid is ethane (CH_3CH_3)*

e) C_2H_5OH *conjugate base is ethoxide ($CH_3CH_2O^-$)*

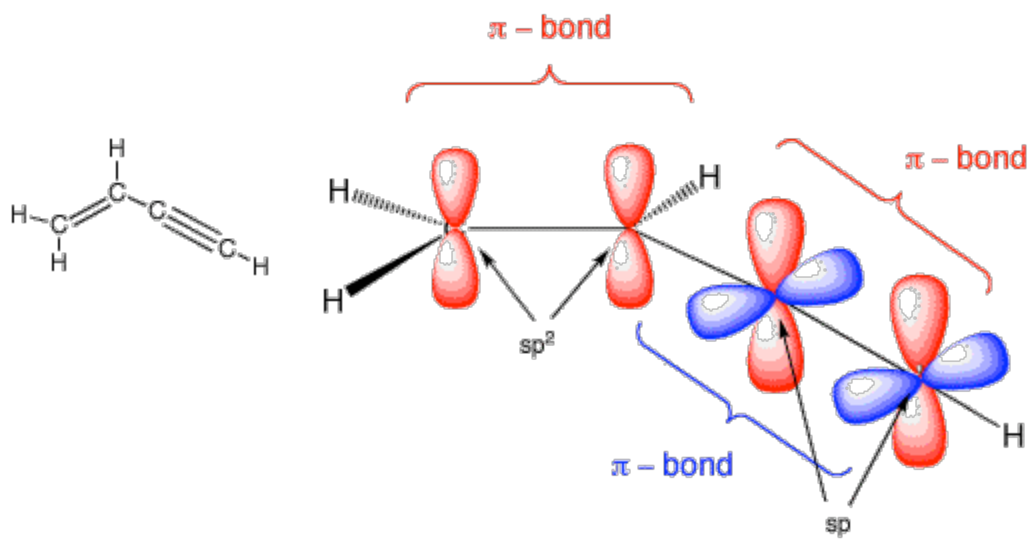
4. Arrange the acids and conjugate acids in problem #3 in order of increasing acidity (decreasing pKa).

Increasing acidity, left to right.

ethane (pKa = ~50), *ammonia (pKa = 35)*,,*ethanol (pKa = 15.9)*, *methanol (pKa = 15.5)*, *acetic acid (pKa = 4.76)*

5. Draw an orbital picture for the monomer, vinylacetylene (CH_2CHCCH). Identify π-bonds and hybridization.

The overall molecule is planar. There are two orthogonal (90^o) π-bonds in the linear triple bond. The red π-bond of the alkyne is conjugated (has resonance) with the red π-bond of the alkene.



6. A normal alkane, C_nH_{2n+2}, is found to have a vapor density of 1.78 mg/mL at 300^oC and 740 mm pressure. Using the ideal gas law, determine the structure of the alkane. (In the early 19th century, the vapor density of an unknown liquid was compared to the vapor density of air to determine the liquids molecular weight.) *Recall from general chemistry the ideal gas law: PV = nRT, where n = g/M; P (atmospheres), V (liters), n (moles), g = (grams), M = MW = (grams/mole), T (temperature in ^oK) and R = (gas constant, 0.0821 l-atm/moles-^oK). Since density (d) = mass/volume; d = g/V. Since PV = nRT or PV = gRT/M, then d = g/V =PM/RT. Transposing, M = dRT/P. At a given temperature and pressure, d is proportional to M by a factor of R. P = 740 mm Hg/760 mm Hg = 0.974 atm.; T = $300^o + 273^o = 573^oK$. M = dRT/P = (1.78) x (0.0821) x (573)/0.974 = 85. 97. M.W. = 86. Based upon the formula, the alkane is a completely saturated, acyclic alkane. There are n carbons at mass 12 and 2n +2 hydrogens at mass 1 in the compound. Therefore, (12)n + [(1)(2n +2)] = 86 or 14n = 84; n = 6. The alkane is C_6H_{14} . Since it is a normal alkane, it is unbranched. Ans: n-hexane.*