Chapter 14

Some Compounds With Oxygen, Sulfur, or a Halogen

Chapter 14 suggested problems: 24, 26, 28, 30, 32, 34, 38, 40, 42, 44, 46, 50, 52, 64, 66, 70, 71

Class Notes

I. Alcohols, phenols, and ethers

  A. Alcohols, phenols, and ethers can be thought of organic-substituted water compounds

    1. Alcohols: ROH

    2. Phenols: PhOH

    3. Ethers: ROR'

  B. Notes

    1. The OH group is a hydroxyl group, not a hydroxide ion (i.e., it is not charged but is covalently bonded)

    2. The O atom is sp^3 hybridized in all three compounds, which impacts molecular geometry around the O atom

    3. Hybridization occurs, even though the number of bonding electrons remains the same, because its results in four orbitals that are lower in energy (i.e., are nearer the nucleus and therefore lower in energy), and because the spatial arrangement of the hybrid orbitals (tetrahedral) results in more favorable distances between the electron pairs than would be the case in unhybridized orbitals (109.5° vs. 90° bond angles)

    4. The two lone pairs results in a distortion of the R-O-R bond angles from 109.5° to ~104.5°

II. Some common alcohols

  A. Methanol - wood alcohol

  B. Ethanol - grain alcohol

  C. Isopropanol - rubbing alcohol

  D. Ethylene glycol

  E. Glycerol (glycerin)

III. Classifying and naming alcohols

A. The reactivity of alcohols depends on the number of carbon atoms bonded to the carbon with the OH group

1. 1°, 2°, and 3° alcohols

B. Nomenclature rules

1. Find the longest chain with the C-OH
2. Change the end of name of the corresponding alkane from "e" to "ol"
3. Keep chain numbers as small as possible
4. Names and numbers of substituents as prefixes
5. Cyclic alcohols: cyclo + backbone name + "ol"
6. Multiple hydroxyl groups: alkane + "diol" or "triol" as is appropriate
7. Diols are also commonly known as glycols

C. Examples

1. 2-heptanol
2. 1,1-diphenyl-2-propanol
3. 3-methyl-1,5-pentanediol
4. cis-1,2-cyclohexanediol
5. 1,3,5-pentanetriol

D. Constitutional isomerism in alcohols

1. Constitutional isomers are a function of two types of connectivity differences
2. Different carbon skeletons
   a. C_4H_{10} and its two isomers
   b. C_5H_{12} and its three isomers
   c. C_6H_{14} and its five isomers
3. Different positions of the hydroxyl group
4. Note that the C:H ratio is unaffected by the presence of an OH group, so the molecular formula can provide limited insight into whether the compound is an alkane, cyclic alkane, or alkene
   a. Hydrogen Deficiency Index = # carbons (tetravalent atoms) - (monovalent atoms/2) + (trivalent atoms/2) + 1

IV. Physical properties of alcohols

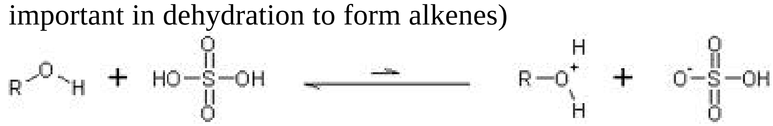
A. The capacity to form hydrogen bonds influences the physical properties of alcohols

substance	BP (°C)	solubility	substance	BP (°C)	solubility
methane	-162	no	methanol	65	yes
ethane	-89	no	ethanol	78	yes
propane	-42	no	1-propanol	97	yes
butane	-1	no	1-butanol	117	moderate
pentane	36	no	1-pentanol	138	slight
hexane	69	no	1-hexanol	158	no

1. Alkanes, alkenes, alkynes, and aromatic compounds are only capable of dispersion interactions
   a. Low BP, MP, insoluble in water and other polar solvents
2. Relative to size, alcohols have higher BP, MP, and are soluble in polar solvents
3. For molecules of similar size, diols and triols have higher BPs and MPs
4. As chain length increases, the effect of dispersion forces on physical properties increases

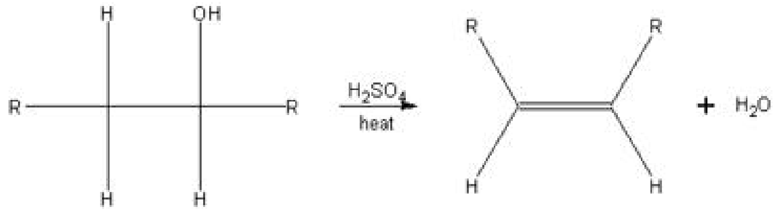
B. The acid/base behavior of alcohols and phenols

1. Alcohols are weakly amphoteric - can behave either as acids or bases, depending on circumstances
2. Alcohols and phenols are mildly acidic due to the high degree of polarity in the O-H bond
3. Alcohols serve as proton donors in the presence of very strong bases (stronger than NaOH), such as sodium metal to form the metal alkoxide and hydrogen gas
4. Alcohols: pK_a similar to that of water (15)
   a. RO^- (alkoxide ion) is a strong base
   b. Solutions of alcohols have a pH of 7
5. Phenol: pK_a similar greater than that of water (10)
   a. PhO^- (phenoxide ion) is also a strong base, but not as strong as most alkoxides
6. Alcohols can be protonated in the presence of concentrated strong acids (only abt. 0.1%, but important in dehydration to form alkenes)



V. Dehydration of alcohols to alkenes (also known as 1,2-elimination reactions or Beta-elimination reactions)

A. The hydroxyl group and an H atom on an adjacent carbon can be eliminated as water (in the presence of a strong acid), resulting in the formation of an alkene



B. While normally there should be an H on a C adjacent to the C-OH, this is not always necessary, e.g. - the dehydration of t-butanol

C. If there are two adjacent carbons with H atoms, Zaitsev's rule applies

   1. The alkene formed in greatest abundance is the one in which H is removed from the adjacent carbon with the fewest H atoms

D. Order of reactivity 3° > 2° > 1° reflects the relative stabilities of both the transition states and the resulting alkenes

E. Factors affecting alkene stability

   1. Degree of substitution: tetrasubstituted > trisubstituted > disubstituted > monosubstituted > unsubstituted

   2. sp^2 hybridized carbons are electron-attracting; electron-releasing groups - such as alkyl groups - tend to stabilize alkenes

   3. Steric strain: trans-disubstituted are generally more stable than cis-disubstituted

F. Zaitsev's rule restated: 1,2-elimination reactions yield the most highly substituted alkene as the major reaction product (true for both E1 and E2 reactions)

G. Examples

   1. 1-pentanol

   2. 2-pentanol

   3. 3-pentanol

   4. 3-methyl-3-pentanol

   5. 2, 3-dimethyl-3-pentanol

   6. 2,2,3-trimethyl-3-pentanol

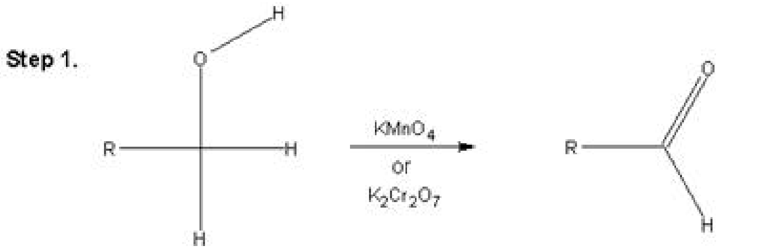
VI. Oxidation of alcohols

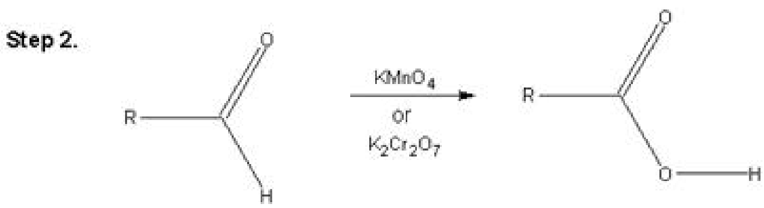
A. Combustion (complete oxidation of all carbons)

B. Selective (mild) oxidation - only the C bonded to the hydroxyl group is oxidized

   1. Potassium permanganate or potassium dichromate can be used

   2. Primary alcohols: two-step oxidation

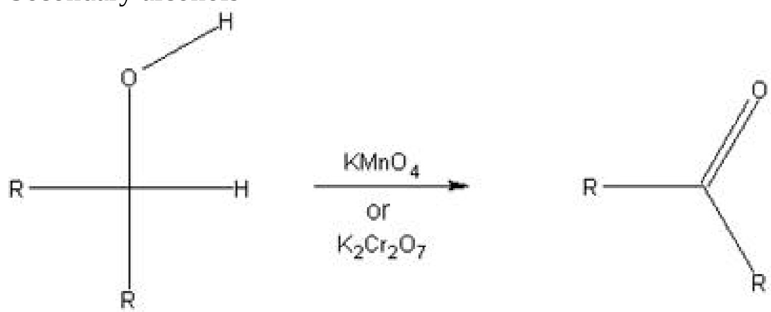




   a. Step 1: simultaneous loss of H from the hydroxyl group and from the C to which the hydroxyl group is bonded, formation of an aldehyde

   b. Step 2: oxidation of the aldehyde H to OH and conversion of aldehyde to carboxylic acid

3. Secondary alcohols



   a. Oxidation can cannot proceed beyond step 1 due to the lack of hydrogen on the carbonyl carbon

4. Tertiary alcohols

   a. Oxidation cannot occur due to lack of H atoms on carbon bonded to hydroxyl group

C. Mild oxidations can be used to qualitatively detect and differentiate between 1°, 2°, and 3° alcohols

VII. Phenols - substituted benzenes - skip

VIII. Ethers

A. General feature: R-O-R, can be aliphatic, aromatic, cyclic

B. Symmetrical and unsymmetrical (mixed) ethers

C. Many substances have more than one ether linkage

1. Diethers: 1,2-dimethoxyethane

2. Triethers (diglyme: diethylene glycol dimethyl ether) and polyethers

D. Nomenclature

1. Alkoxy derivatives of alkanes

   a. Ethoxyethane and diethyl ether

   b. Methoxyethane and ethyl methyl ether

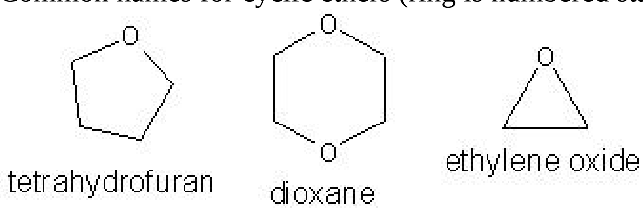
2. Common nomenclature for simple ethers based on names of alkyl groups (given in alphabetical order)

   a. Methyl ethyl ether

   b. Isopropyl phenyl ether

   c. Dibutyl ether

3. Common names for cyclic ethers (ring is numbered starting with the O atom)



E. Constitutional isomers

1. For an ether with a particular molecular formula, there may be other isomeric ethers

2. "Any ether is a constitutional isomer of an alcohol containing the same number of carbons."

F. Physical and chemical properties

1. Polar C-O bonds result in dipole-dipole interactions

2. Higher MP, BP and better solubility in water than alkanes & etc. but not quite as water soluble as alcohols

3. Unreactive toward acids, bases, and oxidizing agents - good solvents for many organic reactions

4. Can be totally oxidized (i.e., combustion)

IX. Formation of ethers by dehydration of alcohols: intermolecular vs. intramolecular dehydration

A. The dehydration of alcohols is an intramolecular dehydration i.e., both the H and the OH come from the same molecule

B. The dehydration of *primary* alcohols (2° and 3° don't work) can result in intermolecular dehydration and the resulting formation of water and an ether

C. The principle difference in reaction conditions is that of temperature (180°C for alkene formation, 120-140°C for ether formation)

D. This will only form symmetrical ethers, there are other ways to form unsymmetrical ethers

X. Thiols and disulfides

A. Alcohol analogues in which an S atom replaces the O atom (i.e., R-SH)

B. Nomenclature - rules much the same as for alcohols

    1. Add the suffix "thiol" to the end of the alkane name without dropping the "e"

        a. 1-butanethiol

        b. 1,3-pentanedithiol

    2. -SH groups as substituents are referred to as mercapto (sulfhydryl) groups

        a. 2-mercaptoethanol

        b. 1,2,4-trimercaptohexane

    3. Used to be called mercaptans but generally abandoned

C. Physical and chemical properties

    1. Lower MW thiols are easy to smell

    2. Polar, but no hydrogen bonding

    3. Weak acids but more acidic than alcohols because the S-H bond is weaker than than O-H bond

D. Disulfides

    1. Thiols are easily oxidized to disulfides 2 R-SH -> R-S-S-R

    2. Disulfides are named based on the alkyl groups

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