普通高等学校21世纪专业英语教材

Organic Chemistry

有机化学

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前　言

化学是一门中心科学，有机化学又是化学的基础性学科。《有机化学》课程是面向大学二年级学生的一门课程，对于培养学生基本化学思维具有关键作用。编者长期从事有机化学的基础性教学与科研工作，并在一段时间有幸承担了多个年级《化学专业英语》的教学工作。在教学中对学生学习专业英语的艰辛深有感触，学生往往耗费大量时间和精力，而结果却不尽如人意。这种体会促使我将《化学专业英语》与《有机化学》糅合起来，开展有机化学双语教学，并将双语教学的宗旨定位在提高学生英语实际应用能力上，从而达到回归语言本质的目的。

这种尝试与教育部提倡的"采用英文原版教材，实施双语教学"精神基本上是相吻合的，实际上，由于教育体制的不同，国外原版外文教材涵盖了我国中学教育的很多内容，这使得其篇幅过大(上千页)，全盘引入不仅造成学生经济上的压力，且在有机化学课程有限的学时内也难以消化。不同的原版教材差异很大，有的比较注重反应机理，而对反应性质的叙述及应用一带而过；有的则在反应性质叙述上占了大量篇幅，这是缘于不同作者对有机化学的理解不同，而国外不同的学校都具有自己相对独立的教学体系，可以根据自己的教育思想自由选择，这与我国现有教学现状是有很大差异的。有机化学课程的教授对象是大学低年级学生，必须考虑由于语言能力而造成的阅读困难。这些因素，使得引进原版教材的教学效果大打折扣，因此，编者在参照国外众多原版教材的基础上，决定结合自己双语教学的长期实践编写一本有机化学英语教材，在内容上既充分展示原版教材的特点，又可以与中国现行的教学体系相吻合，只有这样，才可以扬长避短，取得较好的教学效果，于是就有了本书。

与原版教材相比，此自编教材的优势体现在：

1. 内容精练，在保持语言原汁原味的基础上尽可能简化语言描述层次，使其简单易懂。

2. 综合国外众多知名大学教材，集百家之所长，优势互补，将有机化学最精华的部分展现给读者，使其更加适应中国化学教育体系，包括与中学化学教育接轨的问题，达到既引进先进的教育理念和教学方法，又可与中国教育体系相融合的作用。

3. 按照中国的教育体系适当增加了有机化学反应及其实际应用的分量。

4. 附录B的专业英语词汇便于学生集中学习和检索，附录C摘录了一些常用化学网络数据库站点，供学有余力的学生进一步探索。

本书的出版将为有机化学双语教学提供一种新的尝试，为教学方法改革提供一种思路，希望能起到抛砖引玉的作用，促进双语教学这一新生事物在化学教学领域开花结果，为培养与国

际接轨的一流人才做出贡献。

本书在编撰过程中得到多方支持，湘潭大学出版社朱美香教授、右江民族医学院姚金光副院长、潘小炎教授、刘运广教授、解继胜教授、黄政月科长、韦英群科长等多位专家、老师为本书的出版过程提出了诸多建设性建议并给予了大量帮助，在此谨向他们表示衷心的感谢。

最后感谢您选择本书，希望对您的学习和工作有所帮助。由于编写时间仓促，书中可能会有一些不妥之处，敬请读者指正。

程金生

2007－11－20

CONTENTS

An Introduction to Organic Chemistry

After studying this section, you will (a) understand what is meant by the "structure of an organic compound" and the term "functional group", (b) be able to recognize the structures of alkanes, alkenes, alkynes, haloalkanes, alkanols, carboxylic acids and esters, and (c) understand how a given empirical formula can apply to a number of different isomers.

I What is Organic Chemistry

Organic chemistry is the chemistry of the compounds of carbon, which is combined with many other elements (in particular H, N, O, S, P and the halogens) form over 5 000 000 compounds.

Many of these compounds are of immense importance, as the list below shows:

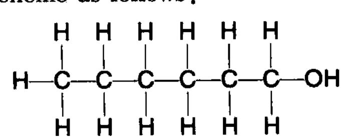
- Fuels
- Solvents
- Explosives
- Detergents
- Plastics, synthetic fibres
- Rubber
- Wool, cotton, natural fibres
- Insecticides, pesticides
- Animal toxins, plant poisons
- Vitamins, hormones
- Synthetic pharmaceuticals
- Antibiotics
- Dyestuffs
- Foodstuffs, flavourings and preservatives

Apart from water, living things are largely made up of organic compounds, notably proteins, fats, carbohydrates and nucleic acids. These compounds are playing an important role in all life processes, which is called biochemistry

II Structure of Organic Compounds

Organic compounds tend to be built according to a general scheme as follows:

The carbon atoms form a "skeleton", in this example, shown on the right, a chain of six C atoms.



One or more reactive chemical groups of atoms (known as functional groups) are attached to the carbon chain (in this case the functional group is —OH).

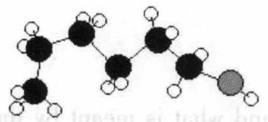
Hydrogen atoms are bound to the carbon skeleton by means of covalent bonds.

There are other ways of representing the structure of organic compounds:

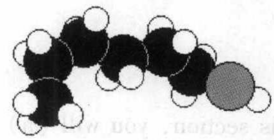
$CH_3CH_2CH_2CH_2CH_2CH_2OH$

represents the same molecule, without bonds being shown.

occasionally only bonds are shown, or one uses models are known as ball-and-stick or filled:

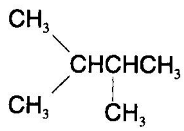


Ball and Stick



Filled

The arrangement in space of all the atoms of a molecule is called the STRUCTURE of the molecule. The complexity of the structure will clearly depend on the molecule.



For example, the structure of the particular substance with formula C_6H_{14} may be described in terms of a STRUCTURAL FORMULA such as the one shown on the left.

III Functional Groups

Functional groups are groups of atoms which have special chemical properties and define the chemistry of an organic compound.

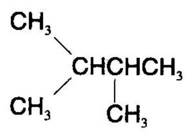
The following are common functional groups:

(none)	alkanes
C═C	alkenes
C≡C	alkynes
C—X (X is a halogen atom)	haloalkanes
C—OH	alkanols
COOH	carboxylic acids
CO—O—C	esters

Alkanes:

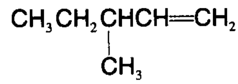
Alkanes are hydrocarbons (compounds containing only C and H) which have single covalent bonds joining the carbon atoms. The carbon atoms form open chains, which may have branches. The molecular formula of all the alkanes fits the expression C_nH_{2n+2}, where n is the number of the carbon atoms.

Check that the formula is C_6H_{14}!



Alkenes:

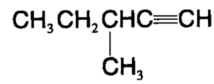
Alkenes are hydrocarbons (compounds containg only C and H) which have one or more C═C double bonds (two C atoms are linked by 4 shared electrons). The general formula is C_nH_{2n}, which is two hydrogen atoms less than the corresponding alkane.



Alkenes are said to be UNSATURATED, (since they do not have their full complement of hydrogen atoms).

Alkynes:

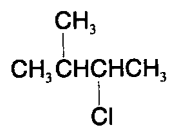
Alkyne are hydrocarbons (compounds containg only C and H) which have one or more triple bond.



Alkynes are said to be UNSATURATED, (since they do not have their full complement of hydrogen atoms). The simplest alkyne, is acetylene.

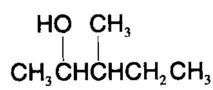
Haloalkanes:

If one or more hydrogen atoms of an alkane is replaced by a halogen atom (chemists use the SUBSTITUTION for this process), this compound is a haloalkane.



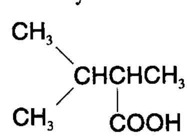
Alkanols:

These compounds arise when one or more hydrogen atoms of an alkane are substituted by the —OH (hydroxyl) functional group.



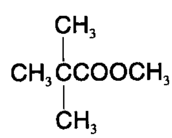
Carboxylic acids:

These compounds have one or more carboxyl —COOH functional groups.



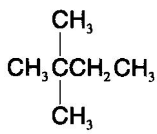
Esters:

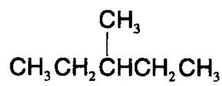
Esters are compounds which have the CO—O—C functional group.



IV Isomerism

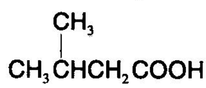
Have a good look at the two structural formulae below. Both of them are structural formulae applying to molecules with molecular formulae C_6H_{14}.

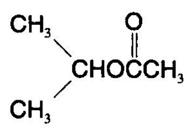




These two molecules are said to be ISOMERS. Isomers are compounds which share the same molecular formula, but different structural formulae. Normally isomers also differ in their chemical and physical properties.

Isomers do not have to belong to the same class of organic compounds. For example, the compounds whose structural formulae are shown below, are isomers. The one on the left is a CARBOXYLIC ACID, where as the one on the right is an ESTER:





Both have the molecular formula $C_5H_{10}O_2$.

Questions

1. Could you give some typical examples of organic compounds in our lives?
2. What's functional group? How many functional groups have you learned?

Chapter 1 Alkanes and Cycloalkanes

Background…

An introduction to the alkanes (including cycloalkanes) and their physical properties.

Burning alkanes…

The combustion of alkanes, including incomplete combustion.

Halogenation…

The reactions between alkanes and chlorine or bromine.

Cracking…

A brief look at cracking alkanes in the oil industry.

1.1 Introduction

This is an introductory paragraph about alkanes such as methane, ethane, propane, butane and the rest. It deals with their formulae and isomerism, their physical properties, and an introduction to their chemical reactivity.

1.1.1 What are alkanes and cycloalkanes

1.1.1.1 Alkanes

(1) Formulae

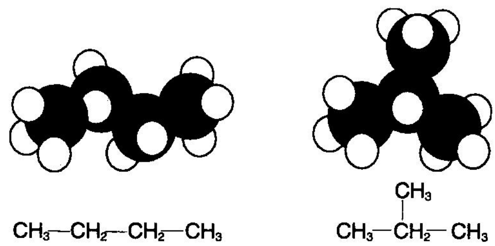
Alkanes are the simplest family of hydrocarbons-compounds containing carbon and hydrogen only. They only contain carbon-hydrogen bonds and carbon-carbon single bonds. The first six are:

methane	CH_4
ethane	C_2H_6
propane	C_3H_8
butane	C_4H_{10}
pentane	C_5H_{12}
hexane	C_6H_{14}

You can work out the formula of any of them by means of C_nH_{2n+2}

(2) Isomerism

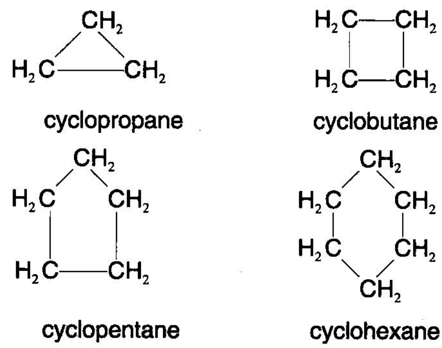
All the alkanes with 4 or more carbon atoms show structural isomerism. It means that there are two or more different structural formulae that you can draw for each molecular formula. As an example, C_4H_{10} could be either of these two different molecules:



These are called butane and 2-methylpropane respectively.

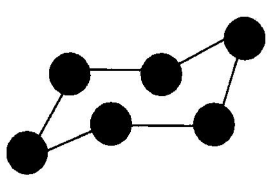
1.1.1.2 Cycloalkanes

Cycloalkanes again only contain carbon-hydrogen bonds and carbon-carbon single bonds, nevertheless, now the carbon atoms are joined up in a ring. The smallest cycloalkane is C.



If you count the carbons and hydrogens, you will see that they no longer fit the general formula C_nH_{2n+2}. By joining the carbon atoms in a ring, you have to lose two hydrogen atoms.

You are unlikely to need it, but the general formula for a cycloalkane is C_nH_{2n}. Don't assume that they are all flat molecules. All the cycloalkanes including cyclopentanes mentioned above exist as "puckered rings". Cyclohexane, for example, has a ring structure which looks like this:



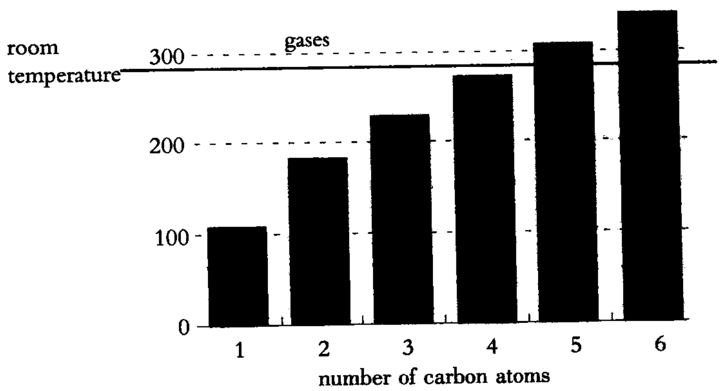
This is known as the "chair" form of cyclohexane——of which shape resembles a chair in a way.

Note: This molecule is constantly changing, with the atom on the left currently pointing down flipping up and the one on the right flipping down. During the process, another (slightly less stable) form of cyclohexane is formed known as the "boat" form. In this arrangement, both of these atoms are either pointing up or down at the same time.

1.1.2 Physical Properties

1.1.2.1 Boiling Points

(1) The facts



The boiling points shown above are all for the "straight chain" structured isomers where of these alkanes.

Notice that the first four alkanes are gases at room temperature. While the C_5 to C_{17} alkanes are liquid. The alkanes with one or more carbon atoms are solids. You can't be more precise than that because each isomer has a different melting and boiling point. By the time you get 17 carbons atoms into an alkane, there are unbelievable numbers of isomers!

Cycloalkanes have boiling points which are about 10 ~ 20 K higher than the corresponding straight chain alkane.

(2) Explanations

There isn't much electronegativity difference between carbon and hydrogen, so there is hardly any bond polarity. The molecules also have very little polarity by themselves. A totally symmetrical molecule like methane is completely non-polar.

It means that the only attractions between one molecule and its neighbours will be Van der Waals dispersion forces. These will be very weak for a molecule like methane, but it will increase as the molecule get bigger. That's why the boiling points of the alkanes increase with molecular size.

For the structural, the more branched the chain, the lower the boiling point tends to be. Van der Waals dispersion forces are smaller for shorter molecules, and only operate over very short distances between one molecule and its neighbours. It is more difficult for high branched molecules (with lots of branching) to lie as close together as the long chain isomer thin ones.

For instance, the boiling points of the three isomers of C_5H_{12} are:

pentane 309.2 K; 2-methylbutane 301.0 K; 2,2-dimethylpropane 282.6 K.

The slightly higher boiling points for the cycloalkanes are presumably because the molecules can get closer together as the ring structure makes them tidier and less "wriggly"!

1.1.2.2 Solubility

(1) **The facts**

What follows applies equally to alkanes and cycloalkanes.

Alkanes are virtually insoluble in water, but dissolve in organic solvents. The liquid alkanes are good solvents for many other covalent compounds.

(2) **Explanations**

(I) Solubility in water

When a molecular substance dissolves in water, you have to

- break the intermolecular forces within the substance. In the case of the alkanes, these are Van der Waals dispersion forces.
- break the intermolecular forces in the water so that the substance can fit between the water molecules. In water the main intermolecular attractions are hydrogen bonds.

The amount of energy to break the Van der Waals dispersion forces in something like methane is pretty negligible, but the amount of energy to break the hydrogen bonds in water is pretty high.

As something of a simplification, a substance will dissolve if there is enough energy released when some new bonds are made between the substance and the water to make up for what is used in breaking the original attractions.

The only new bonds between the alkane and water molecules are Van der Waals attractions. These don't release enough energy to compensate for what you need to break the hydrogen bonds in water. Therefore the alkane doesn't dissolve in water.

Note: This is a simplification in that you also have to consider entropy changes when things dissolve. If you don't yet know about entropy, don't worry about it!

(II) Solubility in organic solvents

In most organic solvents, the main forces of attraction between the solvent molecules are Van der Waals, either dispersion forces or dipole-dipole attractions.

It means that when an alkane dissolves in an organic solvent, you are breaking Van der Waals forces and replacing them by new Van der Waals forces. The two processes more or less cancel each other out energetically, and alkanes are soluble in nonpolar or slightly polar solvents.

1.1.3 Chemical Reactivity

1.1.3.1 Alkanes

Alkanes contain strong carbon-carbon single bonds and strong carbon-hydrogen bonds. The carbon-hydrogen bonds are only very slightly polar and so there aren't any parts of the molecules carrying any significant amount of positive or negative charge which other atoms groups might be attracted to.

Therefore, alkanes have a fairly restricted set of reactions.

You can

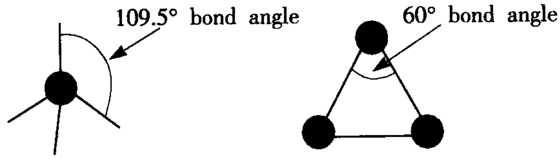
- burn them to destroy the whole molecule;
- react them with some of the halogens, breaking carbon-hydrogen bonds;

- crack them, breaking carbon-carbon bonds.

1.1.3.2 Cycloalkanes

Cycloalkanes are very similar to the alkanes in reactivity except for the very small ones-especially cyclopropane. Cyclopropane is much more reactive than you would expect.

It is due to the bond angles in the ring. Normally, when carbon forms four single bonds, the bond angles are about 109.5°. In cyclopropane, they are 60°.



With the electron pairs closing together, there is a lot of repulsion between the bonding pairs joining the carbon atoms. That makes the bonds easier to break.

We will deal with this later.

1.2 The Combustion of Alkanes and Cycloalkanes

This section deals briefly with the combustion of alkanes and cycloalkanes. In fact, there is very little difference between the two.

1.2.1 Complete combustion

Complete combustion (given sufficient oxygen) of any hydrocarbon produces carbon dioxide and water.

1.2.1.1 Equations

It is quite important that you can write properly balanced equations for these reactions, because they often come up as parts of thermochemistry calculations. Don't try to learn all the equations as there are far too many possibilities. Work them out as you need them.

For example, with propane (C_3H_8), you can balance the carbons and hydrogens as you write the equation down. Your first draft would be:

$$C_3H_8 + O_2 \longrightarrow 3CO_2 + 4H_2O$$

Counting the oxygens leads directly to the final version:

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

With butane (C_4H_{10}), you can again balance the carbons and hydrogens as you write the equation down.

$$C_4H_{10} + O_2 \longrightarrow 4CO_2 + 5H_2O$$

Counting the oxygens leads to a slight problem with 13 on the right-hand side. The simple trick is to allow yourself to have "six-and-a-half" O_2 molecules on the left.

$$C_4H_{10} + 6\frac{1}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$$

If that offends you, double everything:

$$2C_4H_{10} + 13O_2 \longrightarrow 8CO_2 + 10H_2O$$

1.2.1.2 Trends

The hydrocarbons become harder to ignite as the molecules get bigger. This is because the bigger molecules don't vaporise so easily-the reaction is much better if the oxygen and the hydrocarbon are well mixed as gases. If the liquid isn't very volatile, only those molecules on the surface can react with the oxygen.

Bigger molecules have greater Van der Waals attraction which makes it more difficult for them to break away from their neighbours and turn to a gas.

When the combustion is complete, all the hydrocarbons will burn with a blue flame. However, combustion tends to be less complete as the number of carbon atoms in the molecules increases. It means that the bigger the hydrocarbon, the more likely you are to get a yellow, smoky flame.

1.2.2 Incomplete combustion

Incomplete combustion (where there isn't enough oxygen present) can lead to the formation of carbon or carbon monoxide. As a simple way of thinking about it, the hydrogen in the hydrocarbon gets the first chance to combine with the oxygen, and the carbon gets whatever is the left over!

The presence of glowing carbon particles in a flame turns it yellow, and black carbon is often visible in the smoke. Carbon monoxide is produced as a colourless poisonous gas.

Why is carbon monoxide poisonous?

Oxygen is carried around the blood by haemoglobin (US: hemoglobin). Unfortunately carbon monoxide binds to exactly the same site on the haemoglobin that oxygen does.

The difference is that carbon monoxide binds irreversibly-making that particular molecule of haemoglobin useless for carrying oxygen. If you breathe in enough carbon monoxide you will die from a sort of internal suffocation.

1.3 The Halogenation of Alkanes and Cycloalkanes

This section describes the reactions between alkanes and cycloalkanes with the halogens fluorine, chlorine, bromine and iodine-mainly concentrating on chlorine and bromine.

1.3.1 Alkanes

(1) The reaction between alkanes and fluorine

These reactions are explosive even in the cold and dark, and produce carbon and hydrogen fluoride. It is of no particular interest. For example:

$$CH_4 + 2F_2 \longrightarrow C + 4HF$$

(2) The reactions between alkanes and iodine