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LEATHER CHEMISTRY FOR FOREMEN

First Year Course

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PRACTICAL BASIC CHEMISTRY FOR FOREMEN

1st Year

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FOREWORD

This manual is one of a series of three manuals on "Practical Basic Chemistry for Foremen" prepared by the A. C. Lawrence Leather Company, Peabody, Massachusetts, in cooperation with the Department of Leather Chemistry, Lowell Technological Institute, Lowell, Massachusetts.

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TABLE OF CONTENTS

		Page
LECTURE 1	Atoms and Molecules	1
LECTURE 2	Symbols and Formulas	5
LECTURE 3	Some Non-metallic Elements	8
LECTURE 4	Chemical Reactions	13
LECTURE 5	Chemical Arithmetic	18
LECTURE 6	Metals	22
LECTURE 7	Solutions	27
LECTURE 8	Ionization - Part I	32
LECTURE 9	Ionization - Part II	36
LECTURE 10	Atomic Structure	39
LECTURE 11	Introduction - Structural Theory	45
LECTURE 12	Hydrocarbons and Methane Series	51
LECTURE 13	Alcohols	58
LECTURE 14	Aldehydes, Ketones, Acids, Esters	67
LECTURE 15	Fats, Oils and Waxes	77
LECTURE 16	Amines	84

TABLE OF CONTENTS

Page

LECTURE 17 90
Carbohydrates

LECTURE 18 97
Aromatic Amines

LECTURE 19 104
Halogen Compounds

LECTURE 20 112
Dyes and Dyeing

INORGANIC CHEMISTRY

LECTURE 1

ATOMS AND MOLECULES

Science

Man has always demanded an explanation of the facts of nature. By facts of nature we mean those phenomena observable by man's senses: night and day, the change of the seasons, the falling of an unsupported object, sickness and death, fermentation and decay, etc. Early explanations we call superstition. These called on supernatural living creatures, gods, devils, spirits, vampires, and genii. They were supposed to control nature and cause the effects we observe. Modern man explains the same facts by a system we call science. Science has proved a better method because it produces more reliable results. The number of cures of blood-poisoning effected by penicillin (science) is greater than that produced by having your friends beat on kettles to drive out the devils (superstition).

Science is then, a method of explaining and helping us to remember facts. Since it does this by a method called theory (really simplified models to help us visualize things), it is necessary for us to remind ourselves that science deals in facts. We all have a tendency to get so interested in the theories that we forget why we evolved them.

Chemistry

In the early days of science (it was then called Natural Philosophy) the number of facts which had been observed was small. The number of theories needed to explain them was within the ability of one man to know them all. However, as the number of facts known to science grew, it became impossible for one man to know them all, and science was divided. Hence we now have a great number of divisions of science: astronomy, mathematics, chemistry, physics, biology, psychology, and many more. In fact each of these "sciences" has grown until no man knows all about any one.

We are going to talk about Chemistry, the science which deals with the changes which matter undergoes. Chemistry deals with such things as burning of coal, where coal undergoes a change from its original form to ashes and flue gases. It also deals with all other similar changes, e.g. hides to leather.

Matter

If chemistry deals with matter, we must first decide what matter is. The scientist says it is anything which possesses mass, or more simply, anything which has weight. In other words, matter is any material object.

Such things as electricity, heat, light, sound since they do not have weight are not matter. Millions of observations have convinced us that matter cannot be cut up indefinitely. If we take a quart of water we can divide it into two pints, and again into gills, and then into ounces and then into drops, but there is a limit. We cannot divide water into any quantity less than 0.000 000 000 000 000 000 0012 ounces. (That's 1200 millionth millionth millionth millionth of an ounce.) Although this quantity is extremely small it is important that there is a limit. It allows us to think of water as something definite, something with a makeup of its own. We call these tiny quantities of matter which we cannot divide without destroying the matter, molecules.

Molecules

Our first theory, then, is that all matter is composed of tiny particles called molecules. These we cannot divide without destroying the matter. Each kind of matter is composed of a different kind of molecules. Water has one kind of molecules, sugar has a different kind, sulfuric acid has a still different kind, and so on thru all the pure substances. If we mix sugar and water, we get sugar solution. This is not pure water nor is it pure sugar, it is a mixture of two substances so there is a mixture of molecules.

Of course, all this means that there are millions of different kinds of molecules. However, we do have this simplification, all molecules of the same substance are the same. All water molecules are alike, all sugar molecules are alike. This is certainly a fortunate circumstance, for if molecules of a certain substance were not all alike, there would be no sense, no order, no science of chemistry.

Atoms

Now we have said that molecules cannot be divided without destroying the substance. However, if we don't mind destroying the material, there are ways of dividing molecules. Let's go back to our example of water. If we treat water with an electric current we can divide the molecules and when we do, we destroy the water and get in its place two gases, oxygen and hydrogen. This process is sort of like dividing a crowd. If you take a crowd of 100 people, you can divide it up into two crowds of 50 each, of ten crowds of 10, until you get down to one person. Can you divide further? Yes, but the result will not be a person. You begin to get arms, legs, heads, etc. This means that molecules are made up of something smaller and these smaller units are called <u>atoms</u>. Our example of the crowd is still good, for the atoms like the arms and legs have no separate existence. They are parts of molecules but can exist only when combined into molecules. We said above that there are millions of different kinds of molecules. In the case of atoms, we are better off. The chemist has been able to find only a few over 90 different kinds of atoms. (The atomic energy boys at Oak Ridge found a few more but the chemists cannot take any credit for those.) It is because there are so few kinds of atoms that chemistry becomes a science which a man may hope to master. There are only about 90 kinds of atoms and all the millions of kinds of molecules are made by different combinations of the few atoms. Two kinds of molecules will be immediately obvious, vis, those made

of all the same kind of atoms, and those made up of different kinds. Water had two kinds of atoms, oxygen has only one kind.

Elements

When all the atoms in a molecule are alike we call that molecule an Element. This means then, that there can be only around 90 elements. It also means that no matter what chemical process we use we can get only that same kind of atoms out.

Some elements are plentiful on the earth and important to industry; some are scarce and of no importance. Iron, sulfur, oxygen, copper, carbon, chlorine, silver, and gold are examples of elements that are plentiful enough to be important. Krypton, indium, neodymium, dysprosium are rare and of little importance.

Compounds

When the atoms which make up a molecule are of more than one kind we call the resulting substance a compound. The number of possible compounds is infinite, new ones are being made every day. Nylon and some of the new plastics are examples of these new compounds.

Compounds may be composed of two kinds of atoms, or of many. Water is composed of two kinds- oxygen atoms and hydrogen atoms. Sulfuric acid is composed of three different kinds- hydrogen, sulfur, and oxygen. Note that these are compounds because there are present more than one kind of atom in each molecule. It is also worthy of note that the atoms must be in the same molecule, for a compound to exist. Air, for example, contains principally oxygen and nitrogen. It happens tho, that the oxygen atoms are all combined with other oxygens (that is, an element) and the nitrogen atoms are all combined with other nitrogens (another element). Molecules of oxygen and nitrogen in the same molecule do not exist in air. This situation where more than one kind of molecule exists in a substance produces what we call a mixture.

Mixtures

When we talked above about elements and compounds, we were talking about pure substances. A pure substance is one all of whose molecules are alike. It is, of course, possible to mix molecules. The sugar and water mentioned above is an example. These substances are simply called mixtures. They may be mixtures of compounds or mixtures of elements. Air is a mixture of molecules of oxygen and molecules of nitrogen; both are elements.

A great many substances are really mixtures - i.e. composed of more than one kind of molecules. When this happens, there is no chemistry involved in the mixing, the molecules simply lie side by side without affecting each other. If we put sand in the sugar, no action takes place, you have both sand and sugar molecules without change. When you mix a pigment and a binder there is likewise usually no chemical action - a mixture results where the original molecules are still present.

Summary

Chemistry - the science of matter and its changes.

Matter - anything that has weight.

Molecules - smallest particle of matter.

Atoms - building blocks of molecules. No separate existence.

Elements - substances whose molecules contain only one kind of atom. Often 2, 4 or 8 atoms per molecule.

Compounds - substances whose molecules contain more than one kind of atoms. Sometimes only 2 kinds, sometimes a dozen or more kinds.

Mixtures - substances composed of more than one kind of molecules.

Further Reading

Black and Conant - New Practical Chemistry - Chapt. 3, Chapt. 7
Brownlee, Fuller, Whitsit - Elements of Chemistry - Chapt. 1, Chapt. 5

INORGANIC CHEMISTRY

LECTURE 2

SYMBOLS AND FORMULAS

In our last lecture we discussed chemistry and its fundamental building blocks, atoms and molecules. We learned that chemistry was the science that told us about changes in matter.

Before we can talk much about these changes, we need a method of representing them - we need a short hand for writing down chemical information.

Chemical Symbols

Fortunately a very simple and effective method of writing chemical information is available. It works like this - each atom is represented by the initial letter of its name, e.g. C stands for one atom of carbon, O stands for one atom of oxygen. When more than two elements have the same initial letter, we use two letters to distinguish. C stands for cargon, Cl for chlorine, Cr for chromium. Since chemistry is an international science and its symbolism should be international, some symbols are derived from languages other than English. Iron is Fe, tungsten is W, and silver is Ag.

Now there are about 95 different kinds of atoms, 95 different elements. There are, therefore, 95 different symbols. I am passing out a card listing these symbols with some numbers we will need later.

Chemical Formulas

Each symbol represents one atom. Now, if we write two symbols together, they represent a molecule, the chemical union of the two atoms. For instance, the poisonous gas carbon monoxide is a molecule composed of one atom of carbon and one atom of oxygen. The chemist writes this CO. Common salt is made of one atom of sodium and one atom of chlorine - its <u>formula</u> is NaCl. Of course, some molecules contain more than two atoms. We represent this by writing all the atoms side by side. Merchlor or laundry bleach is made of sodium, chlorine, and oxygen atoms. Its formula is NaClO.

When an atom appears more than once in a molecule, we indicate the number of times it appears by writing a subscript after its symbol, as in water which is made of two atoms of hydrogen and one of oxygen. Its formula is H_2O. Sulfuric acid is H_2SO_4. Sodium bicarbonate is $NaHCO_3$.

It is interesting to note here how much the properties change when chemical combination takes place. Carbon is a black solid. Oxygen is a colorless gas, the essential constituent of air. But carbon monoxide CO is

a colorless poisonous gas. Sodium is a soft silvery metal which catches fire when put with water. Chlorine is a green, evil smelling, poisonous gas. But their chemical union NaCl is common salt. This complete change of properties is usual when elements combine to form new molecules.

The elements are, as stated in the last lecture, molecules containing only one kind of atom. Oxygen is O_2, chlorine is Cl_2, sulfur is S_8 and phosphorus is P_4.

Atomic Weights

One of the properties characteristic of an atom is weight. Each atom has a particular weight characteristic of that atom. Of course the actual weights are extremely small, too small to be of practical use, but by assigning a practical size weight to each atom, relative weights are determined which tell us how much heavier one atom is than another. Oxygen is chosen as the standard for these atomic weights. It is assigned the number 16. On the card given you will be found the relative weight, the atomic weight, of each atom.

Molecular Weights

If we add up the weights of all the atoms in a molecule, we get the relative weight of the molecule, or molecular weight. Noting that carbon has atomic weight 12, and oxygen is 16, we see that the molecular weight of CO is 28. Likewise for sulfuric acid, H_2SO_4, we get

$$\begin{array}{lrcl} H & 2 \times 1 & = & 2 \\ S & 1 \times 32 & = & 32 \\ O & 4 \times 16 & = & \underline{64} \\ & & & 98 \end{array}$$

It should be pointed out that altho the atomic weight of oxygen is 16, its molecular weight is 32 because the molecule of oxygen is O_2. The value of these atomic and molecular weights will appear later.

Valence

We have seen above that atoms combine to form molecules, i.e. they have combining power or chemical affinity. It is convenient to measure this combining power and we call this measure of combining power valence. Valence is a measure of the combining power of an atom.

We must have a unit in terms of which to measure any quantity and the unit of combining power - valence - is the combining power of hydrogen. When an element combines with one hydrogen, we say it has a valence of one, when it combines with two hydrogens its valence is 2, etc. Hence chlorine has a valence of 1 for it forms hydrochloric acid, HCl. Oxygen has valence 2 (H_2O), nitrogen is 3 (NH_3, ammonia) and carbon is 4 (CH_4, methane).

A knowledge of valence is most convenient, for it allows us to write formulas without remembering them. For instance, we said chlorine has

valence 1, and oxygen valence 2. Then a compound between chlorine and oxygen would be Cl_2O. The oxygen having twice the valence of chlorine would require two chlorines to satisfy it. Chlorine and nitrogen form NCl_3, and carbon and chlorine give carbon tetrachloride CCl_4.

It requires a little practice to use this idea of valence but it saves the chemist remembering hundreds of formulas. We memorize a few valences and figure out our formulas from them. We should know valences as follows:

H = 1 O = 2 Cl = 1 Na = 1

A few more will be added as we go along.

Summary

Symbols - Each element represented by a letter symbol which stands for one atom of that element.

Formulas

When atoms combine to form molecules, we write the symbols of the elements combining, side by side, indicating presence of more than one of a particular atom by the appropriate subscript.

Atomic Weights

The relative weights of the atoms with oxygen assigned the value 16, are known as atomic weights.

Molecular Weights

The sum of the atomic weights of all the atoms in a molecule is called the molecular weight.

Valence

The measure of the combining power of the atoms, hydrogen taken as unity, is called valence.

INORGANIC CHEMISTRY

LECTURE 3

SOME NON-METALLIC ELEMENTS

Non-metals

The elements we have been discussing the last few weeks are divided into two large classes, metals and non-metals. The classification is rather obvious in most cases. Metals are those elements having the usually acknowledged metallic properties of luster, high melting point, conductivity of heat and electricity, malleability, ductility, etc. Non-metals lack these properties. They are liquids, gases, and some solids. Today we discuss some of the non-metals.

Oxygen

Oxygen is the most important non-metal. It is a colorless, odorless, gas which constitutes one-fifth of the volume of the air. It is also present in most minerals and many organic compounds. It is the most abundant of all the elements.

It is important for two reasons:

1) It is the usual cause of combustion.
2) Its compounds, the oxides, are the basis of so much of inorganic chemistry.

Combustion

When a substance combines with oxygen, and all elements except fluorine, the rare gases, and platinum, do, energy is usually given out. Sometimes this energy is given out in large amounts, carbon for example. If conditions are arranged so that the process takes place rapidly, heat and light are evident and we say the substance burns, combustion takes place.

So combustion is rapid combination with oxygen. Noticable heat and light are given out. Since combustion is such an important source of the world's useful energy, an understanding of the process is most desirable.

Three conditions are necessary for combustion to occur:

1) A substance to burn.
2) A source of oxygen (supporter of combustion we usually call it).
3) The temperature must be raised to a point where the reaction goes on rapidly. This is called the kindling temperature. It varies greatly according to the substance.

Any one of the three necessary conditions may be used to control combustion. In a gas burner we control the combustible substance. In a coal burner we control the supporter of combusion by regulating the drafts. A fire company puts out most fires by putting water on the material and lowering its temperature below the kindling temperatures.

Oxidation

The process of combining with oxygen is called oxidation. Hence combustion is a type of oxidation. Not all oxidation is combustion though. The rusting of iron is oxidation but it does not take place rapidly enough to be classed as oxidation.

Example: Glucose is oxidized when reacted with sodium bichromate to form chrome tan. Heat is developed, which makes the solution boil violently.

Oxides

The product of oxidation of an element is called an oxide. The properties of oxides are very important. Most oxides can be made to combine with water. Some do this by direct mixing, some must be brought to this combination by indirect means. In either case the result is an important chemical compound. If the oxide is that of a metallic element, its compound with water is a base, or alkali. Most of you are familiar with this process in the case of lime. Lime is CaO, the oxide of the metal calcium (calcium oxide). When put with water we have

$$CaO + H_2O = Ca(OH)_2$$

The $Ca(OH)_2$ is calcium hydroxide, a base. (Commercially called slaked lime.)

If the element whose oxide was made to combine with water is a nonmetal, e.g. SO_3, we get an acid

$$SO_3 + H_2O = SO_2(OH)_2$$

$SO_2(OH)_2$, also written H_2SO_4, is an acid (sulfuric acid). Please note that both acids and bases contain the hydroxyl (OH) group. This is pointed out here as it is important and even chemists some times forget it since they usually write acids with all the hydrogen atoms grouped together at the beginning of the formula.

When acids and bases combine they eliminate water and another compound called a salt is formed. Salts usually contain oxygen.

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O$$

As we go along we shall see that oxygen is present in a very great number of compounds both inorganic and organic.

Chlorine

Another important non-metal is chlorine. It is a green, evil smelling, poisonous gas. It is found in nature mostly combined with the metal sodium as sodium chloride ($NaCl$) as common salt.

While chlorine combines with oxygen, its compounds are unstable and mostly explosive and so are of little importance. Its compounds with hydrogen are important. HCl is hydrochloric acid and $HClO$, called hypochlorous acid is the compound resporsible for chlorine bleaching and water purification.

The compounds of chlorine with metals, chlorides, are all but one or two soluble in water When it is desired to get a compound of a metal which will dissolve in water, the chloride is frequently chosen. The abundance of chlorine in common salt makes chlorides quite cheap. $CaCl_2$ is a common soluble salt of calcium, and tin chloride $SnCl_2$ is a much used salt of tin.

Chlorine is reactive in its compounds, i.e. its compounds are not so firmly bound together but what they can be easily broken up by chemical means, hence chlorine compounds are frequently used in reactions.

Sulfur

Sulfur is a yellow brittle odorless solid. It is found in nature both free as the element and combined with metals as sulfides. It is an element of great importance because it is the parent element of sulfuric acid (H_2SO_4), which is the most important acid by far, both commercially and in the laboratory. H_2SO_4 combines all the desirable properties of a strong acid with a very low price. It is used somewhere in almost every chemical process. It is made by preparing sulfur trioxide (SO_3) and dissolving this in water in a process known as the Contact Process.

Nitrogen

Nitrogen, another odorless, colorless gas found in air (about 4/5 by volume) is important because it is an essential requirement of all living matter.

The element itself is not very reactive, but its compounds are all reactive.

The important nitrogen acid, nitric acid (HNO_3) is valuable because it dissolves some metals, copper and silver, which the other commercial acids will not dissolve, and because the salts so formed are all soluble.

Nitrogen compounds are present in all fertilizers.

The chief source of nitrogen is the atmosphere. Nitrogen compounds are made from this great reservoir of nitrogen by processes known as <u>nitrogen fixation</u>.

There is a considerable percent of nitrogen in leather.

Phosphorus

Phosphorus is another non-metal of importance. It is yellow, soft, solid which oxidizes so easily that it must be protected from the oxygen of the air by being kept under water. Another form is a red powder, less easily oxidized. Its chief source is certain rocks found widely distributed over the earth. An excellent supply of one of these ($Ca_3(PO_4)_2$) is found in Florida.

Its most important use is in fertilizers. It is an essential of all plant foods.

It is well known, of course, that matches owe their ability to produce fire to phosphorus.

It forms an acid, phosphoric acid (H_3PO_4) which is of less importance than the others mentioned above.

Allotropic Forms

Some elements form more than one molecule, with the atoms arranged differently. Oxygen forms O_2 (ordinary oxygen) and O_3, ozone. Both are the element oxygen. The difference in their properties is due to the difference in the arrangement of the atoms in the molecules. Such dual personalities are called allotropic forms of the element.

The two forms of phosphorus mentioned above are allotropic forms of that element. The yellow form is P_4. The arrangement of the atoms in the red form is not known.

Usually allotropic forms differ quite a bit in properties.

Summary

Elements divided into metals and non-metals.

Metals have metallic physical properties and their oxides produce Bases when combined with water.

Non-metals do not have metallic properties and their oxides produce Acids when combined with water.

Oxygen - colorless, odorless gas.
Present in air and many other substances.
Most abundant element.
Produces the oxides mentioned above.

Chlorine - green, evil-smelling gas, poisonous.
Present principally in salt.
Produces hydrochloric acid, HCl.
Compounds with metals mostly soluble.
Compounds are reactive.

Sulfur - yellow solid.
Found free and combined in nature.
Source of sulfuric acid, H_2SO_4, the most important acid.

Nitrogen - colorless, odorless gas.
Source, atmosphere.
Element not very reactive.
Compounds very reactive.
Present in all living matter.
Nitric acid, HNO_3, important commercial acid.

Phosphorus - yellow poisonous solid, or red powder.
Found in rocks in nature.
Used in fertilizer and matches.
Forms phosphoric acid, H_3PO_4.

Allotropic Forms - Two or more forms of the same element. The atoms are arranged differently in the molecules in the different allotropes.

INORGANIC CHEMISTRY

LECTURE 4

CHEMICAL REACTIONS

Chemical Changes

We have seen enough chemistry now to stop and consider what happens during a chemical change. The usual statement is that there is a rearrangement of atoms. We developed a shorthand especially to indicate this sort of thing, so let us write some chemical changes in our sumbolism. For instance, what happens when charcoal burns in air? We try it out and find that we get carbon dioxide, so we write

$$C + O_2 = CO_2$$

In other words, charcoal (carbon) combines with oxygen to give carbon dioxide.

Notice that we have produced no new atoms, and lost none, we have merely rearranged atoms. This is perfectly general and universal. Chemical reactions, no matter how involved, are never anything but rearrangements of atoms.

Law of Conservation of Matter

The principle above is stated scientifically in the Law of Conservation of Matter which states-

In a chemical reaction, matter is neither created nor destroyed. The sum of the weights of the reactants exactly equals the sum of the weights of the products.

This law does not hold in an atomic pile nor in an atom bomb, but those actions are atomic physics, not chemistry.

Chemical Reactions

Let us now classify and study some types of chemical reactions.

1. Simple Combination

Two elements combine to form a compound.

$$C + O_2 = CO_2$$

$$2H_2 + O_2 = 2H_2O$$

$$2\,Na + Cl_2 = 2NaCl$$

Note the important balance of these equations, same number of atoms of each type on each side. This, of course, must be so if the Law of Conservation of Mass is to be followed.

In the first equation above, one carbon each side, two atoms of oxygen. In the second, four atoms of hydrogen, two of oxygen each side. Here we could write.

$$H_2 + O_2 = H_2O$$

because that would give us two oxygen atoms (O_2) on the left and only one on the right. Nor could we write

$$H_2 + O = H_2O$$

because that would mean that the oxygen molecule was o, which we know is not true.

A similar situation exists in the third equation where chlorine molecule is Cl_2.

2. Complex Combination

Compounds combine directly with elements or other compounds.

$$CO + Cl_2 = COCl_2$$

$$CaO + CO_2 = CaCO_3$$

$$Na_2O + H_2O = 2NaOH$$

3. Decomposition

Compounds broken down to elements or to simpler compounds.

$$2HgO = 2Hg + O_2$$

$$2KClO_3 = 2KCl + 3O_2$$

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

4. Double Decomposition or Metathesis

Two compounds exchange atoms or groups.

$$NaCl + AgNO_3 = NaNO_3 + AgCl$$

$$KOH + HCL = KCl + HOH$$

$$Al_2(SO_4)_3 + 3Ba(NO_3)_2 = 3BaSO_4 + 2Al(NO_3)_3$$

5. Other Types

Many other types might be classified, but for now we group all others together.

$$BiCl_3 + H_2O = BiOCl + 2HCl$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$$

Causes of Reaction

The true causes of reaction are unknown, but we have a few simple rules on which we can build an idea of why substances react.

Reaction occurs because there is a state of instability in atoms, a state of "unsatisfaction". By combining with other atoms, some of this instability may be removed, the atoms become more nearly satisfied. All such combination is a compromise. Now if an atom has made such a compromise and then later is placed in a situation where a better compromise is possible, reaction occurs. For example, neither oxygen nor carbon is a satisfied atom. Therefore, we can produce a compound, CO, in which each atom is a little better satisfied than along. However, there is room for much improvement. CO can unite with more oxygen to form CO_2, or with chlorine to form $COCl_2$. All chemical reactions may be regarded in this light.

Rules for Reaction

Observation of many reactions has shown that certain rules of thumb apply.

1. Metals, hydrogen, and the NH_4 radical are called positive(+).

2. Non-metals, acid radicals and oxygen are called negative (-).

3. In general reactions occur only between + and -, not between two +'s or two -'s, altho there are exceptions. The most important exception is the oxide of a non-metal where a non-metal (-) combines with oxygen, another-.

4. The positive part of a compound is written first in the formula.

Writing Equations

It is important to point out here, the great difference between a chemical equation and a mathematical equation. A chemical equation is not a device from which new information may be deduced. It is a statement of what we have found out in the laboratory to be true. A chemical equation is a shorthand way of writing down what happens in the lab. It never means much until we have tried the experiment. We may write an equation and wonder if it works, but the lab, not pencil and paper must settle the problem.

With this in mind we can set up a few rules for writing equations.

Step 1. Write reactants and products with atoms properly arranged.

Step 2. Write correct formula for each substance.

Step 3. Balance.

Example - Write reaction between sodium hydroxide and sulfuric acid.

Step 1. Rearrange:
$NaOH + H_2SO_4 = NaSO_4 + HOH$
First part of each is +, Na, H
Last part is - OH, SO_4
Rearrange +'s and -'s.

Step 2. Get correct formulas
$NaOH + H_2SO_4 = Na_2SO_4 + HOH$

From the H_2SO_4 we see that SO_4 has a valence of 2, and we know that Na has valence 1. Hence, Na_2SO_4 is the correct formula. The others are all correct.

Step 3. Balance
$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$

Observation shows us there are two Na atoms on the right, hence there must be two on the left. (2NaOH). There are now two H's and two (OH)'s on the left, hence $2H_2O$ (HOH) on the right.

There is no way to learn how to work with chemical equations except to do it. I am, therefore, including with the notes a number of unfinished equations. If you will take the time to work them out I am sure you will feel at home with similar equations wherever you meet them.

Summary

Chemical Changes - Rearrangements of atoms.

Law of Conservation of Matter

Can neither create nor destroy matter in a chemical reaction. Sum of weights of products equals sum of weights of reactants.

Chemical Reactions-Classification

1. Simple Combination
2. Complex Combination
3. Decomposition
4. Metathesis
5. Other types.

Chemical Reactions-Cause

Compromise to relieve atomic "unsatisfaction"

Chemical Reactions-Rules for

Positives usually combine with negatives, not likes with likes.

Rules for writing equations

1. Rearrange
2. Correct all formulas
3. Balance.

INORGANIC CHEMISTRY

LECTURE 5

CHEMICAL ARITHMETIC

References: Brownlee, Fuller & Whitsit - Chapter VIII
Black & Conant - Chapter IX

One of the things that makes chemistry so valuable to industry is its quantitative nature. Not only can we predict from chemistry what substances we are going to get from a process, but we can say how much we will get.

This is, of course, fairly obvious from our picture of chemical reaction as a rearrangement of atoms. A little close consideration of the methods of calculation seems in order.

Let us consider the simplest possible case.

$$H_2 + Cl_2 = 2HCl$$

We combine chemically one molecule of hydrogen and one molecule of chlorine. The equation shows us that we get two molecules of hydrogen chloride (HCl). Now on the atomic weight scale which we set up a few weeks ago, hydrogen has atomic weight = 1 so H_2 = 2. Chlorine has atomic weight = 35.5 so Cl_2 = 71. The total weight of these atoms is, therefore, 73. These same atoms appear after the reaction, and their weight cannot have changed, hence the weight after reaction must also be 73. If we look at the 2HCl of the equation we find it to be

1 + 35.5 = 36.5 for each HCl or 73 for the 2HCl.

The equation tells us about the reagents and the product both.

There seems to be little need for this kind of calculation in the simple case above. Let us look at a slightly more complicated reaction.

$$CaCO_3 = CaO + CO_2$$

Here we have limestone ($CaCO_3$) heated and made into lime (CaO) and CO_2. We want to know how much lime we get from a quantity of limestone. Again we must add up atomic weights

Ca	= 40	Ca	= 40	C	= 12
C	= 12	O	= 16	2xO	= 32
3xO	= 48		56		44
	100				

Now, of course, in the equation we start out with 100 atomic weight units of calcium carbonate ($CaCO_3$) and we get 56 atomic weight units of lime (calcium oxide) and 44 parts of CO_2. The 44 + 56 must add up to 100 - we knew that all along. However, we now know how the weight is divided up between the calcium oxide and the carbon dioxide; this we did not know before.

Let us consider another case

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

Here we see two molecules of sodium hydroxide (NaOH) reacting with a molecule of sulfuric acid and producing a molecule of sodium sulfate (Na_2SO_4) and 2 H_2O. Here we may need to know not only about the way the products divide up, but also about the reactants.

As in the other cases, let us consider one molecule - say of H_2SO_4. That would add up to 98 units. Now, two molecules of NaOH, each of 40, react with these 98 units. We need 80 units of sodium hydroxide, therefore. After reaction one Na_2SO_4 (142) and two molecules of water (2 x 18 = 36) remain. Summing it all up, 98 molecular units of sulfuric acid react with 80 units of sodium hydroxide and 142 units of sodium sulfate and 36 units of water are produced.

$$98 + 80 = 178 \qquad 142 + 36 = 178$$

When 98 units of H_2SO_4, and 80 units of NaOH are mixed, everything will go according to schedule. What would happen, however, if 98 units of H_2SO_4 were mixed with 90 units of NaOH. When we had 80 units we used up all the H_2SO_4. Now we have 90 units of NaOH and only enough sulfuric acid for 80. There will, therefore, be 10 units of NaOH left over. In other words, no matter how we mix substances, they still must react in certain molecular ratios and adding extra quantities of either will not change the ratios. If we mix 98 parts of H_2SO_4 with only 70 parts of NaOH, what happens? Well, it takes 80 parts to use up 98 parts of sulfuric acid, so 70 parts of NaOH will not be able to react with all 98, and some H_2SO_4 will be left over.

Going back to the reaction where we added 90 parts (that is, 10 parts over the required amount) of NaOH to 98 part of H_2SO_4, the reaction would leave us with 142 parts of Na_2SO_4, 36 parts of water and the 10 parts of NaOH that was extra.

It is important to realize that except in one special case, where the quantities are in exactly the right molecular ratios, one or the other must be in excess and so some of it will be left over.

So far we have considered only molecular weight units, those mythical quantities based on oxygen = 16. Suppose we change from these to some real weights. For instance, we might say all units will be in pounds. Then oxygen = 16 lbs., hydrogen = 1 lb. etc. These weights where real units of weight are used to describe molecules are called mole or molar weights. On this system the pound mole weight of NaOH is 40 lbs., the ton mole weight of water is 18 tons, the ounce mole weight of H_2SO_4 is 98 ounces.

Molecular weight has no units, it is just molecular weight, a number. The mole weight has units - pounds, ounces, whatever we choose to give it.

Suppose we restate our last example in moles. It would read like this: One mole (98 lbs.) of H_2SO_4 reacts with two moles of NaOH (40 x 2 = 80 lbs.) to produce one pound mole (142 lbs.) of Na_2SO_4 and two pound moles (2 x 18 = 36 lbs.) of water. This brings things from the impractical units of molecular weight to the practical units of pounds.

It is obvious that we do not need whole moles in order to have a reaction. The ratio is unchanged if 1/2 mole of H_2SO_4 reacts with 1 mole of NaOH to give 1/2 mole of sodium sulfate and one mole of water. And it works for 1/3, 1/4 or 111/117 moles.

Let us work out a system for finding how any number of pounds, tons, grams or other units react.

Back to the equation:

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

And the problem - How much sodium hydroxide is needed to react with 150 lbs. of sulfuric acid?

First we ask ourselves - how many pound moles of H_2SO_4 in 150 lbs. One mole is 98 lbs., so 150 lbs. is

$$\frac{150}{98} = 1.53 \text{ moles}$$

Next we ask, what is the mole ratio, i.e. how many moles of the required substance does the equation associate with one mole of the given substance? In this case 2 NaOH react with 1 H_2SO_4 so the mole ratio is two. Thus, we will need

$$2 \times 1.53 = 3.06 \text{ moles}$$

of NaOH. Since there are 40 lbs. in one mole of NaOH, we need

$$3.06 \times 40 = 122.4 \text{ lbs.}$$

of NaOH to react with 150 lbs. of sulfuric acid.

This process is used in every case of finding weights from chemical reactions.

Another example: How many pounds of H_2S will be needed to prepare 5 lbs. of Sb_2S_3 according to the reaction

$$3H_2S + 2SbCl_3 = Sb_2S_3 + 6HCl$$

First we figure moles

H_2S	Sb_2S_3
2 x 1 = 2	2 x 122 = 244
1 x 32 = 32	3 x 32 = 96
34	340

The known substance is Sb_2S_3. Five pounds

$$\frac{5}{340} = 0.0147 \text{ moles}$$

Now the mole ratio (how many of the required or unknown per <u>one</u> mole of the known) is gotten by observation of the equation. The known is Sb_2S_3 (known because we know that we want 5 lbs. of it) and it requires $3H_2S$ to produce 1 Sb_2S_3, therefore the mole ratio is 3.

So $0.0147 \times 3 = 0.0441$ moles of H_2S required and

$0.0441 \times 34 = 1.5$ lbs. of H_2S required

The system outlined above has been modified by various "short cuts" which attempt to make the steps above mechanical. Once the fundamental principle has been learned, any system that seems easy to the user may be adopted. However, the principle should be clearly understood before any short cut system is used.

<u>Summary</u>

Chemistry is a quantitative science.

Equations may be used to determine quantities of substances reacting.

Moles - The molecular weight of a substance expressed in actual weight units.

Method -

1. Determine number of moles of known substance by dividing weight by molecular weight.

2. Determine mole ratio- number of unknown molecules associated in the equation with one molecule of the given substance.

3. Multiply moles of known by mole ratio. This gives moles of unknown (sought).

4. Multiply moles of sought by its molecular weight.

INORGANIC CHEMISTRY

LECTURE 6

METALS

It may be recalled that the metals are those elements with "metallic physical properties" and oxides which react with water to form bases.

Metallic Physical Properties

What are these metallic physical properties?

1. Metallic luster

   The shine or luster of a metal is too well known to need describing.

2. Conduction of heat and electricity

   The metals all conduct heat and electricity many times better than any other substances. There are differences in heat conduction between the metals (silver and copper head the list) but even the poorest among the metals, bismuth, is 200 times better than a brick and 1500 times better than soft wood. The differences in electrical conductivity are even greater.

3. Malleability

   Malleability is the property of a substance which allows it to be beaten or rolled into thin sheets. Metal sheets and foils are common, but can you imagine rolling or beating coke (carbon- a typical non-metal) into a thin foil?

4. Ductility

   The ability of a material to be drawn into a wire is called ductility. Most metals are ductile, although a few are quite low in this property. Non-metals, of course, cannot be drawn into a wire.

5. Elasticity

   A substance possessing elasticity may be deformed within limits and spring back to its original form when the deforming force is removed. Metals are elastic.

The properties listed above are the typical metallic properties. Not all metals possess them all, but they all possess some of these properties. Non-metals seldom possess even one.

Formation of Bases

The chemical characteristic of a metal is the reaction of its oxide with water to form a base. All metallic oxides may be united with water to form bases, although only a few will react spontaneously when mixed with water at room temperature.

The bases are the chemical opposites of the acids. They all:

1. Contain hydroxyl (OH) group

2. React with indicators, like litmus, to give the same reaction. Acids give a different reaction with indicators.

3. React with acids to give a salt and water.

4. Have a soapy, slippery feel in strong solution.

Uses of Metals

The data given above pins down and identifies the metals. Now that we know them and a few of their general properties, let us examine the uses to which they are put. These uses are of two kinds, those using the metals themselves, and those using the metallic salts.

Metals

Most uses of the metals themselves depend on the properties of strength, conductivity, elasticity, etc. These uses rightly belong to mechanical engineering so we will say nothing about them. However, the matter of corrosion ought to be considered, and that is definitely a chemical problem. Corrosion is, in fact, such a big chemical problem that it is almost a science in itself.

Corrosion

When metals react chemically with their environment, we call it corrosion. Corrosion may come from simple contact with air or from some corrosive solution. In designing equipment around a plant using chemicals, it is most important to understand the tendency to corrode of each metal used. Iron is well known for its ease of corrosion (rusting) while copper is consider resistant. However, copper will dissolve rapidly in ammonia water, while iron will stand up quite well.

Corrosion by solutions used in vats or flowing through pipes is a relatively simple problem because we know exactly what our problem is. Corrosion by air in a plant is much more complicated. Here the corrosion may be the result of gases in the air, droplets of corrosive liquid, or just air made very moist by steam.

Corrosion by atmospheric oxygen is very slight unless moisture is present. With sufficient moisture present, corrosion occurs with most metals.

Corrosion does, in fact, occur with all except the noble metals. However, some metals protect themselves by the corrosion products. For example, aluminum is very easily corroded by water and air, but if the water is neutral (contains neither acid nor base), the corrosion product forms a water tight coating on the surface which prevents further corrosion. Thus aluminum pipes are now used to conduct distilled water in labs. The green color of copper roofing is due to a similar protective coating of copper carbonate on the surface of the copper.

These coatings are either oxides, carbonates or hydroxides, hence we may get some idea whether a metal will protect itself, by finding out whether its hydroxide and carbonate are soluble. If they are soluble, the metal will corrode readily in air, if they are insoluble the metal may protect itself. It may be, though, that the coating will not be water-tight and not afford protection even though insoluble. Rust on iron is an example of such an insoluble substance which gives no protection- it flakes off.

When we use metal objects in the plant, we should keep in mind this protective coating. If it is dissolved or knocked off mechanically our protection is gone.

Contamination

Another problem connected with metal vats and piping is the contamination of solutions by dissolving of the metal of the container or pipes. For example, if iron is to be avoided in a particular process, iron tanks and piping must not be used if a solution is employed in them which dissolves iron.

Metal Salts

Metals may also be used in the form of their salts. This is truly a chemical problem. The choice of the proper salt to accomplish a purpose depends on a number of factors. Assuming that a particular metal is required, which salt shall we employ, the chloride, the sulfate, the nitrate, the acetate, etc.?

The factors to consider are:

1. Solubility

   The salt chosen must be of the right degree of solubility for the process in hand.

2. Stability

   Certain salts change form faster than others. For example: ferrous sulfate ($FeSO_4$) is quite unstable in ordinary solutions, while ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2$) is quite stable and gives the same effect as far as iron is concerned.

3. Compatibility

   If the other half of the salt reacts with some material in the bath, complications may result. If a sulfate is added to a solution containing calcium, a precipitate of calcium sulfate results. Hence aluminum sulfate (alum) should not be added if calcium is present.

4. Cost

Obviously the least expensive salt should be chosen - this means usually sulfates or chlorides.

Considerations of Some Important Metals

Sodium and Potassium

Very highly reactive with oxygen or water, explosively in fact, hence of no use in mechanical engineering.

All salts of Na and K are soluble. As a result they are most frequently used as the positive part of a salt where the negative part is the one desired. e.g. $NaHCO_3$ (sodium bicarbonate) is added because we want bicarbonate in our bath, not because we want sodium. The same is true of sodium sulfate, borax (sodium borate), sodium hydroxide, etc.

Sodium is much cheaper than potassium, hence usually employed.

Potassium is required in fertilizers. Plants use potassium in their life process.

Sodium salts are apt to pick up water and become caked and sticky, while potassium is less prone to this fault. In some cases it is worht while to employ the more expensive potassium salt to avoid this trouble.

Calcium

Calcium is another metal used only in the form of its salts. It is too unstable to be used as a metal. It must be kept under oil or it will be changed to the oxide by the air. Its principal use is as the hydroxide ($Ca(OH)_2$). This is the cheapest strong base and is used wherever in the chemical industries a strong base is needed and the calcium is not objectionable. Otherwise the more expensive sodium hydroxide must be used. Calcium compounds are important in the building trades, being essential parts of mortar, plaster, and cement.

Aluminum

Aluminum is used as a structural metal because of its lightness. Weight for weight it is stronger than steel, not volume for volume though.

The metal is quite reactive but it is saved from corrosion by its tough insoluble hydroxide. It cannot be used in solutions other than neutral or the hydroxide will dissolve and expose the metal.

The important salt of aluminum is alum - $Al_2(SO_4)_3$.

Iron

Obviously iron is the most important structural metal. In its usual form it is very easily corroded, hence where corrosion is a problem, as it is in a tannery, iron is usually found in the form of stainless steel if it comes in contact with solutions.

Iron compounds are a problem in a tannery because the compounds of iron are dark colored and insoluble. If iron compounds get on a hide and it is tanned, a dark stain of iron compound is formed.

In some other industries cheaper iron sulfate is replacing alum.

Chromium

Chromium is a very stable metal, hence its use in chrome plating of auto trim, etc. It is difficult to work and expensive, so it is used mostly as a plating on other bases or in alloys like stainless steel, not as a structural base material.

Chrome solutions are of such importance in the tanning of leather that we ought to talk more about the chemistry of chrome than most.

Chromium is an element with many valences. In its lower valences it behaves as a typical metal, forming sulfates, chlorides, etc. In its higher valences, particularly valence 6, it acts as a non-metal and chromium rioxide (CrO_3) dissolves in water forming chromic acid (H_2CrO_4) and dichromic acid ($H_2Cr_2O_7$).

The sodium and potassium salts of this latter acid are the most common salts of chromium. The sodium salt being much cheaper is the chromium salt of commerce. This $Na_2Cr_2O_7$ is used directly in the dye industry, chrome plating, the manufacture of certain pigments, etc.

For chrome tanning we need, however, the metallic form of chromium. Since our best commercial source of chromium salts is sodium dichromate, we need to change this to the chromium type. It is done by adding any one of several substances which are capable of reducing the valence from 3 to 6. I believe here you use glucose and sulfuric acid. The result of this reaction - difficult to write because glucose is a complicated organic substance - is to produce $Cr(OH)SO_4$. This is a mixed salt. One valence of the three of Cr goes to the OH, and two to the SO_4. This is the green material used in chrome tan.

Other Metals

This discussion of metals could go on indefinitely. Out time is so limited that we will have to depend on the book for most of the details.

No mention of metallurgy, the process of getting metals from ore has been made. It makes a very interesting study.

The following chapters are particularly recommended for your reading and study:

Brownlee, et al - Chapters XXVIII and XXIX; also chapters on the metals; XXIII, XXX, XXXI.

Black and Conant - Chapters XXXI, XXXIII, XXXIV and XXIC, XXVII, XXXII.

INORGANIC CHEMISTRY

LECTURE 7

SOLUTIONS

Definitions

Solution - Usually defined as a "Homogeneous mixture of two or more substances". By homogeneous we mean that no matter how searchingly we investigate a solution, we find all parts exactly alike. This is not true of an ordinary mixture.

Solvent - In many solutions one component, usually present in larger quantity, seems to act as the dissolving medium while the other disappears into it. The dissolving medium is called the solvent. When sugar dissolves in water, the water is the solvent. The sugar in this case is the

Solute - The material which disappears or dissolves is called the solute.

When a solid dissolves in a liquid, there is no difficulty in determining that the liquid is the solvent and the solid the solute. However, when one liquid dissolves in another, the distinction between solvent and solute can no longer be made so easily. There is really no difference which we call solvent and which solute. Usually when one is present in large quantity, and the other in small quantity, that in large quantity is called solvent and the less plentiful is considered the solute.

Types of Solutions

We are much more familiar with liquid solutions than with any other kind. However, we may have solutions which are gas, liquid, or solid.

Air might be considered a solution of oxygen in nitrogen (gas in gas). Then on a damp day when humidity is high, water dissolves in the air. This would be liquid in gas. (Solvent air, solute water.)

Examples of solid dissolved in gas are hard to find. Perhaps we could call the disappearance of a moth ball into air, solution of a solid in gas. On the other hand maybe the moth ball turns to gas and the gas dissolves.

Liquid solutions are easy.

Soda water	- Solute CO_2	Solvent water
Sea water	- Solute NaCl	Solvent water
Wine	- Solute alcohol	Solvent water

Solid solutions are again less familiar.

Hydrogen dissolves in the rare metal palladium to give a true solution of gas in solid. Carbon monoxide dissolves in red hot iron.

Liquid in solid solution occurs when leather picks up moisture on a damp day.

Solid in solid is typified by a number of alloys.

Uses of Solutions

When we were talking about combustion, we saw that mixing was necessary before reaction could take place. Since in a solution, the material is extremely finely divided, many times down to individual molecules, solutions offer the ideal method of mixing two substances for chemical reactions. Hence solutions are used as a means of promoting reaction by allowing intimate mixing of the reacting substances.

Solutions have another important use when small quantities of a substance are needed. Suppose we must add 1/10 ounce of an enzyme to a bath. Weighing out this small amount would be bad enough but how to get it mixed all through the bath. However, if we dissolve an ounce on 10 gallons of water and then add one gallon to the bath, we have the 1/10 ounce and it can be distributed through the bath more evenly.

Many other uses could be cited, but these are the main ones.

Saturation

If we start with a quart of water and add salt a little at a time, we find each new addition dissolves, up to a limit. Beyond that limit, no matter how much salt we add, the solution will not become stronger. We say it is saturated.

Let us look a little more closely at this phenomenon. Suppose we drop a large crystal of a substance in a dish of water. Molecules of the substance must leave the surface of the crystal and dissolve. But, we know that there is also a tendency of the molecules of a solute to reprecipitate on the crystal. The rate of dissolving is determined by the substance of which the crystal is made and the temperature. The rate of reprecipitation is determined by the strength of the solution. As the solution gets more and more concentrated the rate of precipitation increases until finally it equals the rate of dissolving. Now the solution can get no stronger. We have a state of equilibrium. A solution of strength is said to be saturated.

A solution less concentrated than saturated is called <u>unsaturated</u>.

Effect of Temperature

Solutions of solid in liquid are usually more soluble as the temperature is raised. Some are many times more soluble in hot water than in cold, some only a little. Potassium nitrate (KNO_3) is over ten times as soluble in hot water as it is in cold; salt (NaCl), on the other hand, increases only about 10 per cent. A few substances are less soluble in hot water. These are mostly calcium salts.

Solutions of gases in liquids are always more soluble in cold water than in hot. This is why a can of warm beer (CO_2 dissolved in liquid) squirts when opened, while a cold can does not.

Supersaturation

Most solids are more soluble when hot. If we prepare a hot solution nearly saturated, and then cool it, the excess solid usually precipitates out as the solution cools off. However, this depends on two conditions. First, crystal seeds must form, then grow as the solute precipitates on them. There are some substances which seem to have difficulty forming crystal seeds. When this happens, there is nowhere for the solid to precipitate and it stays in solution. The solution when cooled is stronger than a saturated solution. It is supersaturated. It will precipitate very quickly if a crystal is added. Supersaturated solutions can only be made by cooling, never by adding more solute. Why?

Strength of Solutions

Many systems of describing the strength of a solution have been devised. A few need discussion here.

Per cent

When a person speaks of a 10% solution and says no more, he tells us practically nothing about the strength. This is because 10% usually means that when you add one unit of volume you add 10% of one unit of weight. For example, a chemist speaks of a 10% solution, meaning that 1 liter (volume) of solution contains 1/10 kilogram (weight) of solute. A dyer, however, speaking of a 10% solution usually means 1/10 ounce per gallon.

Molar

This confusion has led chemists to adopt a more rigorous system.

A molar solution is one containing 1 mole per liter of solution. This is not 1 mole per liter of water, because when you add one mole of solute to one liter of water you have usually more than one liter of solution. Hence to make a molar solution you add one mole of solute to say 800 cc of water and after it has dissolved, you add enough water to make a liter.

The molar solution is a definite and rigorous method of describing concentration of solutions. It is used only by chemists. In other fields confusion still exists. It is best, therefore, to state concentration in unambiguous terms, such as "1 oz. per gal.", or "10 lbs. per 150 gal. vat", etc.

Form of Solute

Most true solutions have the solute dispersed as individual molecules or ions (to be discussed later) surrounded by the solvent. However, there are

some solutions in which multiple molecules are dispersed. Benzoic acid, for example, forms double molecules in benzene and iodine has a tendency to double up in water but not in chloroform. This phenomenon is known as association.

When the degree of association becomes very great, several hundred or thousand molecules, we get what are called colloidal solutions. These are half-way between true solutions and suspensions. Colloidal solutions do not settle out as do suspensions, but the particles are large enough to be seen in many cases. Soaps, dyes and some enzymes form colloidal solutions.

References: Brownlee, et al "Elements of Chemistry" - Secs. 25-28, pp 34-38.
Black & Conant "New Practical Chemistry" - Chapt. XXVI, p 372 et seq.

Summary

Solution

Homogeneous mixture of two or more substances.

Solvent

The dispersing medium of a solution.

Solute

The dispersed substance of a solution.

Solutions may be mixtures of any combination of phases, gas, liquid, or solid.

Uses

Solutions give complete dispersion and mixing.
Solutions allow accurage measurement of minute quantities.

Saturated Solution

One of a strength to be in equilibrium with undissolved solute.

Unsaturated Solution

Weaker than a saturated solution.

Supersaturated Solution

Stronger than a saturated solution.

Temperature and Solutions

Solids usually dissolve better as the temperature is increased.
Gases always dissolve better at lower temperatures.

Preparation of Supersaturated Solution

Prepared by cooling a saturated solution, taking care that there are no crystals present to start precipitation. Not all substances can be prepared in supersaturated solution.

Strength of Solutions

Per Cent - Variable term, to be defined in each case.
Molar - One mole dissolved in enough solvent to make one liter of final solution.

Association

More than one molecule in a group.

Colloidal Solution

Very large groups of molecules held halfway between solution and suspension.

INORGANIC CHEMISTRY

LECTURE 8

IONIZATION - PART I

Last week we discussed solutions. We must now investigate a condition which solutions make obvious. This condition, known as ionization, exists in other situations, but is very noticeable in solutions.

Ions

Certain atoms, when they combine, become electrically charged. In this charged condition they are known as ions. For example, when sodium and chlorine combine to form sodium chloride, the sodium atom becomes positively charge and the chlorine becomes negatively charged. The amount of positive and negative charge is equal, so the salt appears neutral. It is this charge which holds the sodium and chlorine together. Unlike charges attract so the two ions are held together. However, since all positive charges are alike, and all negative charges are alike, a sodium atom is not attracted to any particular chlorine atom. In fact solid NaCl is a collection of alternating sodium and chloride ions. There are no real molecules of sodium chloride. All true inorganic salts are composed of ions. The number of charges carried by an ion is equal to its valence. Thus, sodium ion has a single charge (valence one) and is written Na^+. A chloride ion (valence one) has a single charge and is written Cl^-. A positive valence has a positive charge, a negative valence a negative charge. Calcium ion (valence +2) has two positive charges and is written Ca^{++}. Sulfate ion would be written $(SO_4)^{--}$ Aluminum ion is Al^{+++}, etc.

Solution of Ionizing Substances

When ionizing substances are dissolved, it is the ions which forms the entities in solution. Sodium chloride solution contains Na^+ and Cl^- but no NaCl. In fact, when we write NaCl we are writing the formula for a molecule which really does not exist at all. Substances like salt which are made of ions, behave in solution like a mixture of + and - ions, which indeed they are. This is different from the behavior of substances like sugar or alcohol which are true molecules.

Electrolysis

If wires connected to a battery are dipped into an ionizing solution, these wires will take on a charge from the battery. Now, since unlike charges attract, the positive ions of the solutions will be attracted to the negative wire, and the negative ions will be attracted to the positive wire. Let us suppose two platinum wires with one end of each attached to a

battery and the other ends dipped in a solution of copper chloride ($CuCl_2$). This solution is that of a salt and hence a mixture of Cu^{++} and Cl^-, twice as many Cl^- as Cu^{++}. The negative wire will attract to it the Cu^{++} ions. When they touch the wire, which is negatively charged, they will have their positive charges neutralized. They will become copper. This copper will plate out on the wire. In the mean time negative Cl^- ions have been attracted to the positive wire. There they are neutralized (lose their negative charge) and become chlorine. But chlorine is a gas and as it plates out on the wire it forms bubbles and finally bubbles up through the solution. The copper chloride has been subjected to electrolysis, or electrolyzed. Since only ionic substances can do this, they are frequently called electrolytes.

Strong and Weak Electrolytes

The substances about which we have been talking, salts and bases, are composed of ions. These substances must give a maximum number of ions immediately on dissolving. They are called strong electrolytes.

There is another smaller class of compounds not composed of ions, but which nevertheless can produce some ions when dissolved in proper solvents. Mercuric chloride ($HgCl_2$), which seems at first to be a true salt is found not to have salt properties, but to be composed of molecules of $HgCl_2$. When it is dissolved in water it does produce a few ions. Most of the compound remains in molecular form. Since it produces only a small number of ions, not the large number of a true salt, it is called a weak electrolyte. Ammonium hydroxide (NH_4OH) is another weak electrolyte. The most obvious distinction between weak and strong electrolytes is the ease with which the strong electrolytes conduct electricity, and the relative difficulty with which the weak conduct the current.

Acids

Acids are a class of compounds related to true electrolytes but quite individual in behavior. They are not ionic compounds. They consist entirely of molecules and the perfectly pure compounds contain no ions at all. However, they react chemically with water and a few other solvents to give ions, thus

$$HCl + H_2O = H_3O^+ + Cl^-$$

Here hydrogen chloride reacts with water to give hydronium ion (H_3O^+) and chloride ion (Cl^-). All acids behave in a similar manner. Some produce strong electrolytes in this manner, some weak.

The properties which we associate with an acid are those of the H_3O^+ ion. These are sour taste, red reaction with litmus, reactions with bases or rather with the $(OH)^-$ ion of a base.

Some chemists write H_3O^+ whenever they refer to the acid ion and some shorten it to H^+. However, it is understood that there is no such thing really as H^+. We write it that way for convenience as we write NaCl even though we know there is no molecule of NaCl and we should probably write Na^+Cl^-.

Reactions Between Ions

When a solution containing ions is mixed with a solution containing different ions, all ions of unlike charge attract each other. However, if soluble combinations are produced, the ions remain in solution and nothing really happens. Thus, NaCl solution is Na^+ and Cl^-, KNO_3 solution is K^+ and $(NO_3)^-$. If these two solutions are mixed, Na^+ is attracted to Cl^- and to $(NO_3)^-$ but all sodium salts are soluble so they remain as ions. In like manner K^+ is attracted to Cl^- and $(NO_3)^-$. Here again all remain as ions because all potassium salts are soluble. All we have produced is a mixture of four ions in the solution.

If one of the possibilities is insoluble, however, it will precipitate out and we get a real reaction. E.g. NaCl + $AgNO_3$

$$Na^+ + Cl^- + Ag^+ + (NO_3)^-$$

Here again Na^+ is attracted to the two negative ions and the possible sodium salts are soluble. Nothing happens. But when Ag^+ is attracted to Cl^-, insoluble AgCl is produced. This precipitates out and is removed from the solution. This is the way electrolytes usually react.

There is another possiblity of reaction between electrolytes. If one of the combinations of ions produces a nonionizing substance, it will be formed and ions removed. The most common nonionizing substance to be so formed is water. Water is not completely nonionizing, but it produces so few ions that for most purposes it may be considered nonionizing. In the reaction between sodium hydroxide and hydrochloric acid, ions are

$$Na^+ + (OH)^- + H_3O + Cl^-$$

The only possibility for real reaction is

$$H_3O^+ + (OH)^- = 2H_2O$$

The H_2O does not ionize appreciably, hence removes the hydronium and hydroxide ions from the sphere of action. This is what really happens then when an acid is neutralized by a base.

In the lectures which follow we shall learn more about neutralization and about the ionization of water.

Summary

Ions	- are charged atoms or radicals. The charges they carry are equal in sign and number to their valence.
Salts	- are composed of ions and not molecules.
Electrolysis	- the passage of current through the solution of an ionizing solution and the breaking up of the substance into its elements.

Electrolytes	- since ionizing substances can be subjected to electrolysis, they are frequently called electrolytes.
Strong Electrolytes	- are those which produce the maximum number of ions and pass an electric current freely.
Weak Electrolytes	- are those which produce only a few ions from a normally not ionized substance. They conduct electricity poorly.
Acids	- are molecular substances which react with water to produce H_3O^+ ion, hydronium ion.
Reaction between electrolytes	- occurs only when insoluble or nonionizing substances are produced.

References: Brownlee, et al "Elements of Chemistry" - Chapt. IX, XI.
Black & Conant "New Practical Chemistry" - Chapt. XII, XIII.

INORGANIC CHEMISTRY

LECTURE 9

IONIZATION - PART II

In our previous consideration of ionizations, we learned what ionization is and some of the phenomena associated with it. Today we shall continue our study of this most important theory.

Ionization of Water

We said in our previous discussion that water was a molecular substance which ionized a little. It ionizes a litte, but this little is of great importance. Pure water ionizes

$$2\ H_2O = H_3O^+ + OH^-$$

It will be noted that the ions are hydronium, the acid ion, and hydroxide, the base ion. These are produced in equal quantities, hence water is neutral, neither acidic nor basic.

The ionization of water is characterized by another characteristic. The produce of the concentration of the hydronium ions and the hydroxide ions is constant. The concentration is measured in moles per liter, or rather gram ions per liter for they are not molecules. The product is

$$(\text{conc. } H_3O^+) \times (\text{conc } OH^-) = 0.00000000000001$$

This may also be written

$$\frac{1}{100{,}000{,}000{,}000{,}000}$$

or one one hundred trillienth. Another shorter way of writing it is

$$\frac{1}{10^{14}}$$

Now we noted that pure water produced an equal number of H_3O^+ and OH^- ions. The product of their concentrations must be the figure given above. Since they must be equal, the figure will have to be.

$$\text{Conc } H_3O^+ = \frac{1}{10^7}$$

$$\text{Conc } OH^- = \frac{1}{10^7}$$

$$(\text{conc. } H_3O^+) \times (\text{conc. } OH^-) = \frac{1}{10^7} \times \frac{1}{10^7} = \frac{1}{10^{14}}$$

Now if we add acid to the water, it will ionize to give e.g.

$$HCl + H_2O = H_3O^+ + Cl^-$$

This means that a lot of H_3O^+ ions are added to the water but no OH^-. The product of H_3O^+ and OH^- must remain constant, hence since the acid we added brought the conc H_3O^+ up to 1/10, then the conc OH^- must have dropped to $1/10^{13}$.

In other words, we can make only one choice. If we fix the concentration of the H_3O^+, the concentration of the OH^- can have only one value. Conversely, if we fix the value of the OH^-, the H_3O^+ will adjust itself to make the product $1/10^{14}$.

pH

Since the concentration of the H_3O^+ and OH^- ions in a solution is so important, a simplified scale of indicating it has been perfected.

The scale is called the pH scale and it works like this. A solution is said to have a pH value which is the value of the exponent of ten in the denominator of the fraction representing its concentration. If the pH is 2, then the concentration of H_3O^+ is $1/10^2$. If the pH is 8, then the conc. H_3O^+ is $1/10^8$. If the hydronium ion has a concentration of $1/10^4$, the pH is 4.

Now a neutral solution is one where the concentration of H_3O^+ equals the concentration of the OH^-, and this can be true only when they are both equal to $1/10^7$. The pH of a neutral solution is therefore 7. If we increase the concentration of H_3O^+, say to $1/10^4$, so the pH is 4, the concentration of the OH^- goes down to $1/10^{10}$. This solution has more hydronium ions than hydroxyl, so it is acid. In fact any solution of pH less than 7 is acid, and the smaller the pH, the more acid the solution.

If we add NaOH to increase the OH^- ion concentration, the H_3O^+ ion concentration will have to decrease to some number less than $1/10^7$ e.g. $1/10^{10}$. Thus values of pH greater than 7 are basic, and the larger the number, the more basic they are.

Measurement of pH

pH has turned out to be one of the most significant measurements of chemistry. Living organisms are particularly sensitive to changes in pH. The serious disease called "acidosis" is a condition in which the pH of the blood decreases. It is often fatal. Leather, a product of animal life, is also very sensitive to pH. The amount of swelling and many other properties of untanned hides depends on the pH.

Because of the importance of pH, much research has been done on methods of measurement. The most accurate method of pH measurement is an electrical one. The method is very general and accurate but the apparatus is expensive and delicate.

For cheaper, less accurate measurements, certain dyes have been made which change color gradually as pH changes. This is the most generally used method of pH measurement. It has the disadvantage that it cannot be used on colored solutions.

Buffers

Certain substances, always weak electrolytes, have the property of resisting changes in the pH of their solutions. These substances are known as buffers. The commonest buffers are bicarbonate ($NaHCO_3$ and $KHCO_3$), phosphates (Na_2HPO_4 and NaH_2PO_4) and borates (H_3BO_3 and $Na_2B_4O_7$). A solution containing a buffer will change its pH very little even if acid or base is added. A solution without a buffer will have the pH changed very easily by small additions of acid or base. Strong electrolytes like salts do not act as buffers.

Summary

Pure water ionizes a little, giving H_3O^+ and OH^- ions.
The product of the concentration of H_3O^+ x concentration of OH^- is constant, and equal to $1/10^{14}$.
pH is a short method of indicating conc. H_3O^{+-}.
pH 7 is neutral.
pH less than 7 is acid.
pH more than 7 is basic.
pH can be accurately measured by electrical methods.
A rough measurement of pH may be made with indicators.
Buffers are substances which resist changes in pH.
Buffers are weak electrolytes.

References

Brownlee, et al - Chapt. XI, Appendix Chapt. XII
Black & Conant - Chapt. XII

INORGANIC CHEMISTRY

LECTURE 10

ATOMIC STRUCTURE

The atom bomb has made everybody somewhat conversant with the ideas of atomic structure. The information we have received from this source has been quite specialized and it might be a good idea to see what atomic structure theory has of interest to the chemist.

The Periodic Table

Back in 1869, just after the Civil War, a Russian chemist named Mendeleef made a most remarkable discovery. This was, that the elements, if arranged in order of ascending atomic weights, showed a remarkable periodic recurrence of properties every eight elements. In this arrangement the very similar elements Cl, Br, and I, fell in one column: Ca, Sr, Ba, in another and Li, Na, K, and Cs in another. There are many other examples. In as much as the elements were throught of as individual, unrelated entities at this time, the result was most remarkable. There could be only one conclusion- the elements were in some way related. What this relation could be, no one dared to guess, but a relation must be there. The elements didn't just happen, there must be a system.

Atomic Numbers

No hint of the relationship was more revealing than that produced by Moseley in 1913. He was experimenting with X-rays. These rays are produced when a stream of electrons falls on a metal in a vacuum. Moseley discovered that X-rays of different frequencies were produced by different metals. If the square root of the frequencies produced by different metals were plotted in a graph against the position of the element on Mendeleeff's table, a straight line resulted. Now when two quantities plot as a straight line on a graph, some simple mathematical, numerical, relationship exists. Moseley had found part of the answer to Mendeleeff's puzzle. The relationship between the elements was numerical.

Cathode Rays and Electrons

A number of scientists at the Cavendish Laboratory in England had been working on the rays produced in a highly evacuated tube. These were called cathode rays. The work extended over twenty years. Time does not permit telling much about this work, but a few parts lead directly to the further solving of our puzzle.

These cathode rays were found to be composed of negative electricity. The negative electrical particles were called electrons. It was further shown that the electrons came from the gas in the tube, and that they were all the same no matter what the gas. Subsequent work proved that electrons were constituents of all substances. These atoms contained electrons, all of which were alike. A common component of matter, electrons, had been discovered.

Since atoms are neutral, and electrons are negative, there should be a positive part left behind. This was discovered by Aston.

Atomic Structure

Now that it was known that atoms were composed of positive and negative electricity, a tremendous amount of work was undertaken to determine how they were arranged in the atom. Skipping over the many less satisfactory theories, the present picture is something like this.

The atom is composed of a small center, containing all the positive charges. The number of positive charges is equal to the atomic number and is the thing which characterizes a particular element. You can change anything about an atom except the number of positive charges, and it is still that element. Further, even if you leave everything else the same, if you change the number of positive charges, called protons, you change the element This small positive center is called the nucleus. Besides the protons, the nucleus may also contain a number of neutral particles called neutrons. Both protons and neutrons are relatively heavy (each having a weight equal to one atomic weight unit).

Around this nucleus at a relatively great distance are the electrons. They are moving around the nucleus like planets around the sun in eliptical orbits. The number of electrons in a normal atom is equal to the number of protons.

Thus, hydrogen with atomic number 1 and atomic weight 1, has a nucleus composed of just a single proton. Around this proton rotates a single electron. The weight of the electron is so small that it does not change the molecular weight enough to be determined. (The electron weighs about 1/2000 of an atomic weight unit.)

Chlorine with atomic weight 35 and atomic number 17 has 17 protons and 18 electrons. The weight of 35 being made up of the sum of the weights of the protons and the neutrons. Around this nucleus rotate 17 electrons.

Electron Shells

The arrangement of the electrons is most important to the chemist. Hydrogen has, as we have said only one electron, rotating at a relatively great distance from the nucleus. Helium has atomic number 2, so it should have 2 electrons. These rotate at about the same distance from the nucleus.

When we go to lithium, atomic number 3, we find two electrons placed as in helium but the third is in a region much further removed from the nucleus. It is usually said that the electrons are grouped in Shells. The first shell contains two electrons when full. The second shell eight, the third eighteen, etc. A shell may have less than its full quota, but never more.

The Rare Gases

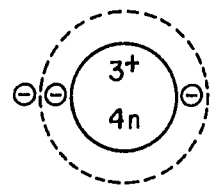
We have mentioned from time to time the rare gases. These elements have valence zero. They do not combine with any other element. When we examine their atomic structure, we find they are the elements with complete electron shells. All other elements have at least one incomplete shell. Chemical action- valence- must, therefore, be associated with incomplete or unfilled electron shells.

Electrovalence

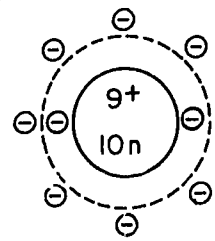
A study of the properties of elements and of their atomic structures leads us to the conclusion that valence or chemical combination is the result of a tendency of atoms to form compromises which give them complete electron shells.

Let us examine one such compromise.

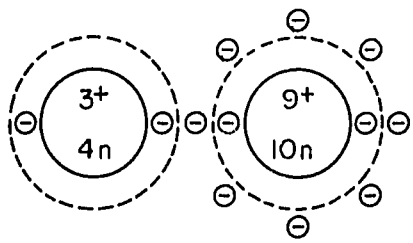
Lithium has an atomic number of 3. Its structure is, therefore, like this:



Fluorine has atomic number 9. Its structure is:



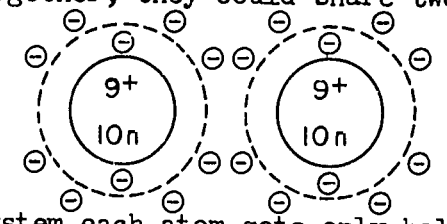
It will be noted that lithium has an outside shell containing only one electron. This shell would be complete with eight. However, if it could get rid of this one electron, it would have a complete shell (2) on the outside. Fluorine has an outside shell of 7 electrons. If it could gain an electron, it would have a complete outside shell of 8. The compromise consists, therefore, in the transfer of one electron from the lithium to the fluorine. They then look like this:



Each becomes electrically charged. Lithium becomes Li^+, an ion; and fluorine becomes F^-, an ion. This is how electrolytes are formed. It is called an electrovalent union. It always produces ions.

Covalence

Another form of compromise occurs when both atoms lack an electron. The formation of fluorine molecule is an example. Above we have shown that fluorine lacks an electron in its outside shell. If two fluorines moved close enough together, they could share two electrons like this:



Of course, by this system each atom gets only half time use of the shared electrons, but apparently it is better to have a full outer shell, part of the electrons of which are shared, than to have a partly filled shell with all electrons full time. This type of union is called covalent union or covalence. The electrons are always shared in pairs. Molecules are produced by this type of union.

There are other types of compromise by which atoms satisfy their urge to complete their outer shells, but time does not permit their discussion here. The two discussed above are the most important.

Radioactivity

All the phenomena which we have discussed so far have dealt with the outer electron shells, not with the nucleus. The electrons are responsible for all the chemical properties of atoms. The properties referred to as radioactive come from the nucleus.

As previously stated the nucleus is composed of protons and neutrons. The number of protons determines the atomic number and the identity of the atom. Let it be repeated that as long as you have a certain number of protons, you have a certain element.

These protons in the nucleus are positive. Now like charges repel, so the protons, all packed in the very small nucleus, tend to repel each other. It seems to be the neutrons which hold the protons together. No nucleus if more than one proton is known without neutrons. Most of the 92 natural elements have the correct number of neutrons in the nucleus to give a stable structure. A few, uranium, thorium, etc. have a nucleus which is unstable. When a nucleus is unstable it tries to reach stability by various means.

Alpha Rays

One method of reaching stability is to eject some of the nuclear material. The ejected material is usually a particle composed of two neutrons and two protons. It is called an alpha particle or alpha ray. Since protons

are taken from the nucleus by this means, a new element is formed which has an atomic number two less than the parent element. Uranium uses this device of alpha ray ejection to overcome its instability. The resulting element has atomic number 90 (uranium has 92) and is thorium. The expedient is, however, not a success and the new thorium is even less stable than the parent uranium. Another alpha particle is given off and another new element produced. Its atomic number is 88 and it is known as radium.

Beta Rays

Another way in which a nucleus may attempt to become more stable is by destroying a neutron in the nucleus. When this happens, the neutron breaks up into a proton and an electron. The proton remains in the nucleus and the electron is ejected. The result is one more proton in the nucleus. The atomic number is increased by one unit. A new element is produced having an atomic number one greater than the parent. The electrons ejected are called beta rays.

Gamma Rays

When alpha and beta rays are produced, it often happens that energy is left over. This energy appears as a ray similar to X-rays and called gamma rays. These have no effect on the elements from which they are produced.

Artificial Radioactivity

The phenomena described above are all natural occurrences. They occur in uranium, thorium, radium, and a few other elements. It is possible to make other elements radioactive by artificial means.

If a stream of neutrons is directed at an element, some of them will strike and be absorbed by the nucleus of the target atom. That means that the element has its balance of protons and neutrons disturbed, and it becomes radioactive. Sulfur has atomic number 16 and atomic weight 32. Its nucleus, therefore, contains 16 neutrons and 16 protons. It is possible to put sulfur in a stream of neutrons and get another kind of sulfur with 16 protons and 19 neutrons. This sulfur is radioactive. It gives off beta rays.

Isotopes

When two forms of an element are known having the same number of protons but different numbers of neutrons like the two sulfurs above, they are called isotopes. Many elements have several stable isotopes. These are usually mixed in the natural form of the element. Chlorine has two such isotopes. One has 17 protons and 18 neutrons, the other 17 protons and 20 neutrons. These two isotopes of chlorine are mixed in nature in such a proportion that the atomic weight of the mixture is 35.46 (One is 35, the other 37.)

Fission

Sometimes when a nucleus is bombarded with neutrons, the resulting nucleus is so unstable that the methods of relief described above, alpha and beta ray ejection, are not enough. These nuclei break approximately in half. This breaking in half of the nucelus is called fission. One of the products of fission is more neutrons and another is a very large amount of energy. The neutrons break up still more nuclei and the energy is available for bombs or atomic power plants.

Summary

Elements are related as indicated by the Periodic Table.

Elements differ numerically as indicated by Moseley's atomic number work.

Elements are electrical. Positive electricity is located in the center nucleus, negative in the outer electrons.

Electrons are arranged in shells in the atom.

Atoms have a great preference for complete shells.

Chemical union, valence, is the result of compromises by which elements attain complete outer shells.

Electrovalence is exchange of electrons.

Covalence is sharing pairs of electrons.

Radioactivity is the result of nuclear unstability.

Alpha rays are groups of 2 protons and 2 neutrons, ejected by radioactive atoms.

Beta rays are streams of electrons, ejected by radioactive atoms.

Gamma rays are similar to X-rays. They result from energy left over in radioactive change.

Artificial radioactivity results when nuclei pick up neutrons or other particles and become unstable.

Isotopes are atoms of same atomic number and different atomic weight, or same number of protons and different number of neutrons.

Fission is the result of a nucleus picking up a neutron and becoming so unstable that it breaks approximately in half.

ORGANIC CHEMISTRY

LECTURE 11

INTRODUCTION - STRUCTURAL THEORY

Early Definition

Up to a century ago substances of mineral origin were classed as "inorganic"; those of animal or vegetable origin were classed as "organic". It was believed that organic compounds had some kind of "vital" or "Life force", which made it seem quite impossible that a chemist could ever hope to reproduce an "organic" substance in the laboratory.

This entire theory was destroyed by the work of a great German chemist Wohler, who in 1828 succeeded in preparing urea in his laboratory by heating ammonium cyanate. Now urea is a true organic compound, for it is the chief end product of the decomposition of proteins in the body and is the chief nitrogeneous constituent of the urine.

It was not long before other chemists were synthesizing acetic acid, fats, alcohol, oxalic acid, oil of bitter almonds, indigo and many other compounds.

Present Day Definition

We still retain the words "organic" and "inorganic" though we no longer think of them in the time-honored sense. What we call "organic" chemistry may more aptly be called the "Chemistry of the carbon compounds", for that is just what "organic" chemistry deals with.

But in reality we do not draw the line too sharply. Such compounds as carbon dioxide, carbon monoxide, carbon disulfide, hydrogen cyanide and the carbonates are usually included in texts on inorganic chemistry, though, of course they are carbon compounds, and according to the definition should be included under "organic" chemistry.

Similarity to Inorganic Chemistry

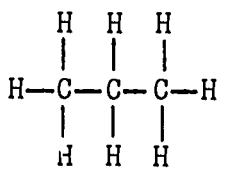
The fundamental laws of chemistry, which the class has taken up in its course of inorganic chemistry, apply to organic chemistry with equal or perhaps greater force. If, then, the dividing line between "organic" and "inorganic" chemistry is not a sharp one, why the necessity for having these two subdivisions?

The Characteristics of Organic Chemistry

1. The number of compounds of carbon known today exceed 500,000 and the number of compounds which do not contain carbon are only about 75,000.

2. In general, organic and inorganic compounds show marked differences in solubility, the former being usually soluble in ether, alcohol, chloroform, benzene, etc. while the latter (inorganics) are not. Whereas many of the inorganic compounds are soluble in water and the inorganic ones are not.

3. The atoms of carbon have the unique property of combining with one another to form chain-like structures - a property not frequently shown by other elements:- for example,



4. Organic compounds are, as a rule, less stable than inorganic; they are much more easily susceptible to chemical and physical changes. Organic compounds are decomposed at relatively low temperatures.

5. "Type" reactions are quite frequent in organic chemistry. For example, there are hundreds of compounds which react with nitric acid to form "nitro" compounds, hundreds of which react with reducing agents to yield "amino" compounds.

6. There is often a marked difference in the velocity of reaction. The change of one organic compound to another is usually a relatively slow process, whereas the transformation of inorganic substances is often practically instantaneous.

7. Reactions in organic chemistry are, as a rule, mostly non-ionic, the solutions being non-conductors of electricity; whereas reactions in inorganic chemistry are largely ionic. This explains the following:

$$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$$

but

$$CCl_4 + AgNO_3 \rightarrow \text{no precipitate}$$

However, organic acids, bases and salts do ionize but to a much lesser degree than their inorganic counterparts.

8. Reactions in organic chemistry often tend to become quite complex, and there are possibilities of many "side" or "secondary" reactions.

9. The complexity in structure exhibited by some organic compounds is quite unknown among inorganic compounds.

10. Organic compounds often show a property called "isomerism" which will be discussed later in greater detail.

Sources of Organic Compounds

A. Organic compounds may be traced either to the plant or animal kingdom. Out of carbon dioxide, water and various constituents from the soil, in the presence of light, the plant builds a very large number of substances: sugar, starches, cellulose, alkaloids (morphine in opium - nicotine in tobacco), acids (citric and tartaric), salts (tartar in grapes), esters (flavoring substances of fruits), dyes (indigo, logwood) and tannin (from nutgalls, etc.).

B. Plants and animals furnish us with fats, proteins, carbohydrates, enzymes and vitamins.

C. Destructive distillation of coal - When soft coal is strongly heated in a retort, this complex substance breaks down into a number of (chemically) simpler substances. The conversion of a complex substance into a number of simpler substances by the aid of heat (in the absence of air) is known as "destructive distillation". The destructive distillation of coal yields coal gas (illuminating gas), ammonia, coke and coal tar. Coal tar at one time discarded as a useless by-product, is now the starting point for any number of organic products (about 225); such as toluene, benzene, naphthalene, anthracene, carbolic acid, the cresols, etc.

D. Destructive distillation of wood - The important products obtained from wood are acetic acid, methanol (wood alcohol, acetone, wood tar, combustible gases and charcoal.)

E. Destructive distillation of bones - This yields animal charcoal (bone black) and bone oil which yields a large number of nitrogeneous compounds, such as: pyridine and quinoline.

F. Fractional distillation of petroleum - (A mixture of two or more liquids having different boiling points may usually be separated from one another by a process of distillation, the liquid with the lower boiling point distilling over first). In the oil industry this yields such products as naphtha, gasoline, kerosene, gas oil, lubricating oil, cylinder oil, vaseline, etc.

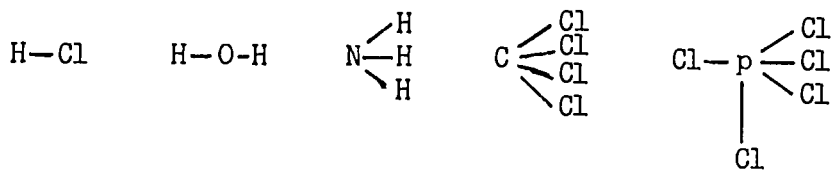
G. Fermentation - Is was for a long time supposed that in the conversion of sugar into alcohol by means of yeast, the living cells of the yeast were primarily responsible for the change. We now know that what brings about this change is not the cells themselves, but substances produced by the cells, known as "enzymes".

Changes analogous to the conversion of sugar into alcohol are known as "fermentation". The sweet apple juice turns to cider (due to the formation of alcohol), and finally to cider vinegar (due to the oxidation of the alcohol into acetic acid). Milk on standing, or when "inoculated" with bacteria, becomes sour (due to the conversion of lactose - milk sugar - to lactic acid).

H. Putrefaction - Putrefaction may be defined as the decomposition of animal or vegetable substances brought about largely by microorganisms, resulting in diverse products, some of which have a foul odor, such as amines, fatty acids, ammonia, hydrogen sulfide, methane, etc.

Valence and Structure in Inorganic Chemistry

Our studies in inorganic chemistry have led us to define valence as the number of atoms of hydrogen with which one atom of an element combines or replaces. To show such relationships graphically in any compound, we indicate valencies by lines or "bonds", each line representing one valency. Thus:



Where not only are hydrogen, oxygen, nitrogen, carbon and phosphorus shown to be mono-, di-, tri-, tetra-, and pentavalent elements respectively, but these valencies are indicated by bonds, each bond representing one valency.

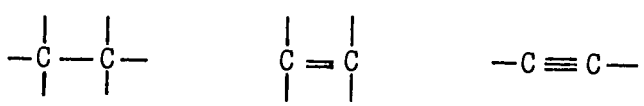
In organic chemistry the use of graphic formulas is very extensive. The distinguishing features of a compound can thus be brought out at a glance, for instance:- HNO_3 is the formula for nitric acid alone, but C_2H_6O stands for grain alcohol or methyl ether. Thus although the molecular formulas are the same, the physical and chemical properties are different.

The Fundamental Bases Underlying the Structural Theory of Organic Chemistry

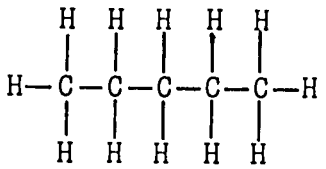
1. The valence of carbon almost without exception, is four, and is represented as:

where any one bond bears exactly the same relationship to the carbon atom as any other bond. These valencies may be represented as directed towards the corners of a regular tetrahedron, constructed around the carbon atom as a center, and are, therefore, equidistant from each other in space.

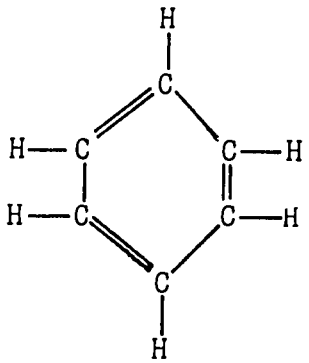
2. Carbon atoms may be united either by single, double or triple bonds.



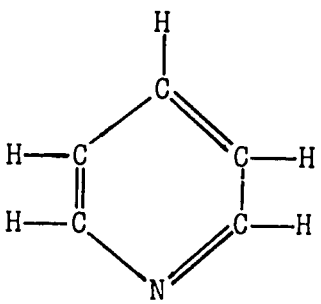
3. Carbon atoms may form a straight chain, for example:



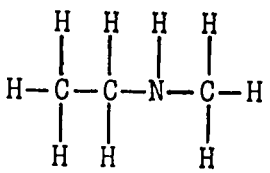
4. Carbon atoms may form a "closed" chain:



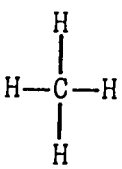
5. Other elements besides carbon may enter a carbon chain or ring:

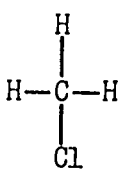


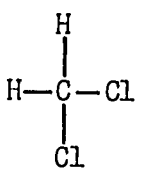
or

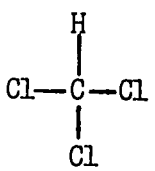


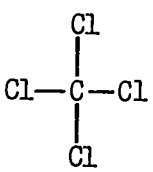
6. Elements may substitute one another in compounds; that is, one element in a compound may be removed, and another may take its place; for example:

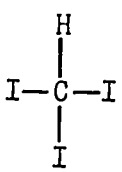


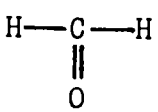




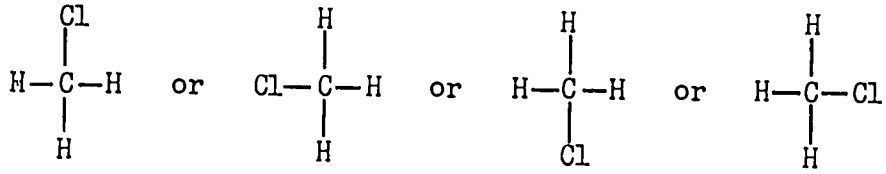






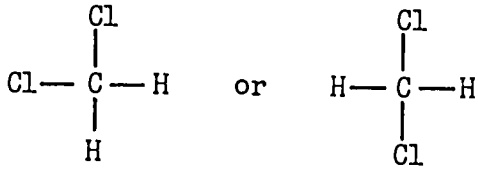


The configuration, or relative location of the four hydrogens of methane, for instance, has no significance due to the fact that our formula is two dimensional, while the molecule in space is three dimensional. Thus it does not matter how we write the formula for mon-chloromethane, for instance:



for they all represent one and the same compound.

Also, if two hydrogen atoms are replaced by two chlorine atoms:



We still have the same compound in either case - dichloromethane.

ORGANIC CHEMISTRY

LECTURE 12

HYDROCARBONS AND METHANE SERIES

Classes of Organic Compounds

The enormous number of organic compounds demands that for purposes of study they must be divided into groups. Based on chemical structure and reactions, two main groups of organic compounds are recognized.

1. The aliphatic or non-benzenoid compounds.

2. The aromatic or benzenoid compounds.

The dividing line between the two classes is not always sharply drawn. The compounds of each group are subdivided into several classes of compounds.

In aliphatic compounds the carbon atoms are commonly linked together in a chain in such a way that the end carbons are not joined to form a ring. Certain compounds which have a cyclic or ring structure are classed as aliphatic compounds because they lack the benzenoid character.

In aromatic or benzenoid compounds the carbon atoms are joined in the ring-like formation that is exhibited by benzene, the basic hydrocarbon of this group.

Plan of Study

In studying the individual organic compounds, those of the aliphatic group will be considered first. The important members of each series will be studied, their occurrence, structure, preparation, properties and in some cases uses. A consideration of the aromatic compounds on the same general plan will follow.

An attempt to study the thousands of known organic would be almost hopeless if each compound had to be considered separately. Fortunately these compounds can be classified under several different general types, and the properties of the members of each type are quite similar. A good idea of the mode of preparation, physical properties and chemical deportment of all the members of a group can be gained by studying a few of its members in detail.

Reactions between Molecules

Many, if not most, of reactions with which we shall deal in organic chemistry probably involve a direct interaction between two different kinds of molecules which must actually collide before they can react. Most slow

reactions are capable of being catalyzed by contact catalysts and many will not take place in the absence of all catalysts. This indicates that simple collision between two molecules is often not enough to initiate a reaction.

The ionic types of reaction involving acids, bases and salts are always extremely rapid; those with more complex mechanisms which involve collision between molecules, between molecules and ions, etc., may have any speed depending on the reactivity of the molecules and the conditions under which they collide.

Saturated Hydrocarbons or Methane Series

A hydrocarbon is a compound which contains hydrogen and carbon. Saturated means that all of the possible valencies have been satisfied, or fulfilled.

This series derives its name from its first and simplest member methane, CH_4. The hydrocarbons of the methane series, sometimes called paraffins, are found in abundance in petroleum and natural gas.

They are formed by the decay, fermentation, or destructive distillation of many kinds of organic matter.

Methane Series

Name	Empirical Formula	Boiling Point 760 m.m.	Melting Point
Gases	$4=2C+2$		
Methane	CH_4	- 161.5	- 184
Ethane	C_2H_6	- 88.3	- 172
Propane	C_3H_8	- 44.5	- 189.9
Butane	C_4H_{10}	0.6	- 135.0
Liquids			
Pentane	C_5H_{12}	36.2	- 131.5
Heptane	C_7H_{16}	98.4	- 90.5
Octane	C_8H_{18}	125.8	- 56.5
Decane	$C_{10}H_{22}$	174.0	- 32.0
Solids			
Hexadecane	$C_{16}H_{34}$	287.5	20
Tetracosane	$C_{24}H_{50}$	243.0 (15 m.m.)	51.1
Hexacontane	$C_{60}H_{22}$		79.4

The above lists a few of this series and indicates the ascendency of properties with increase in molecular weight or molecular size. It is also true that the chemical reactivity varies with the size of the molecule. The smaller members are the most reactive and the reactivity decreases with increase in size. However, in general, the reactions which one member of the series will undergo also apply to all the other members of the series, with the above reservation. Thus, we should be able to set up some general reactions for this series.

General Methods of Preparation

1. $R\ \boxed{COONa + NaO}\ H \longrightarrow RH + Na_2CO_3$

$CH_3\ \boxed{COONa + NaO}\ H \longrightarrow CH_4 + Na_2CO_3$

2. $R\ \boxed{X + 2Na + X}\ R \longrightarrow R\text{-}R + 2NaX$

$C_2H_5I + 2Na + IC_2H_5 \longrightarrow C_4H_{10} + 2NaI$

3. $R\ \boxed{X + H}\ H \longrightarrow RH + HX$

$C_2H_5Br + H_2 \longrightarrow C_2H_6 + HBr$

In the above R refers to any radical such as CH_3-, C_2H_5- C_4H_9- etc. It is shorthand for the chemist to save time. It also indicates that the reaction applies to many compounds, that is, it is general. The letter X is generally used to denote any of the halides, such as Cl, Br, I or F.

General Properties

The paraffins (methane series) are insoluble in water, also lighter than water. They are soluble in alcohol, ether, chloroform, benzene, etc. They are flammable.

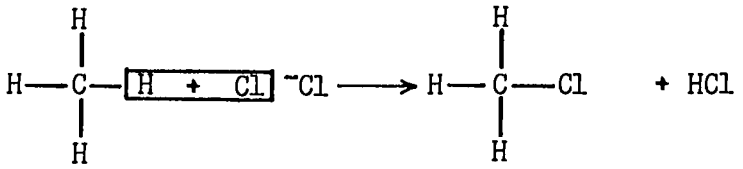
General Chemical Properties

All the paraffins are very stable and inactive. At ordinary temperature they are not acted upon by nitric, sulfuric, hydrochloric or chromic acids. Chlorine reacts in sunlight to form substitution products. Bromine reacts less readily. Iodine does not react at all.

In recent years, however, by the use of high temperatures, pressure and catalysts it has become possible to split the long chain paraffins into two or more smaller chains. Thus, it has been possible to increase the available amounts of the more valuable members of the methane series.

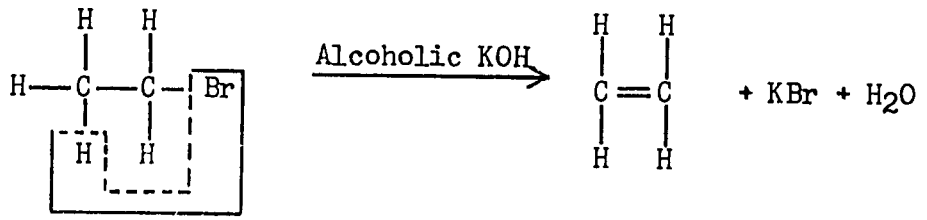
Unsaturated Hydrocarbons

In the previous series, known as the alkanes, all of the four valences of carbon were satisfied, or combined. In this the next series, known as the Olefins or Alkenes, two or more of the carbons are connected by double bonds. In the methane series it was not possible for a new atom to attach itself to the molecule except by substitution. That is, it had to replace one of the hydrogens already there. viz

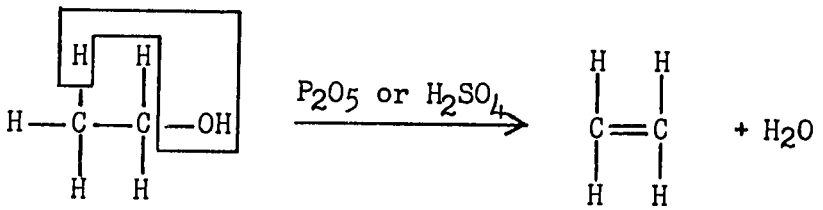


However, in this new series, the alkenes, it is possible to have additions to the double bond or bonds present. The presence of double bonds indicates unstability, potential for chemical reaction and again any reaction typical of one member of the series is usually typical of all the series in varying degrees.

The first member of the alkenes is ethylene. It can be prepared by two methods.

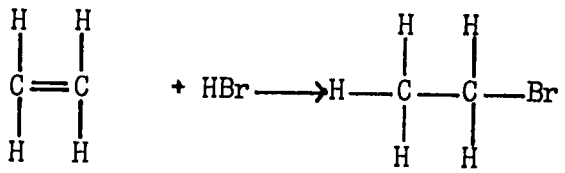
1. 

Ethyl Bromide Ethylene

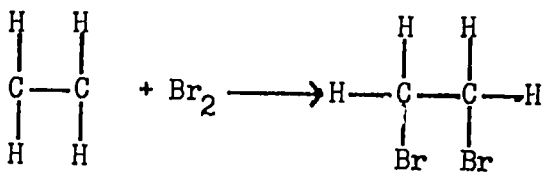
2. 

Ethyl Alcohol Ethylene

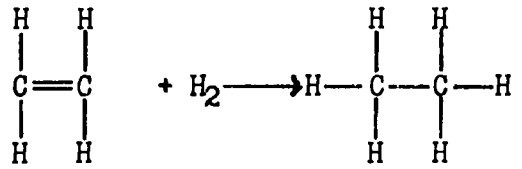
The following reactions with ethylene are indicative of the rest of the series:



Hydrogen Bromide Ethyl Bromide or Bromo Ethane

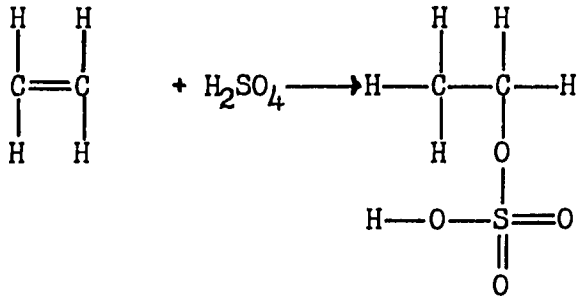


Bromine Ethylene Bromide or dibromoethane



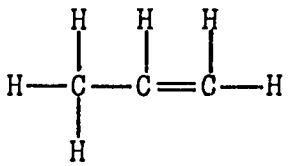
Hydrogen

Ethane

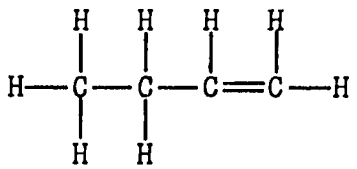


Ethyl hydrogen sulfate

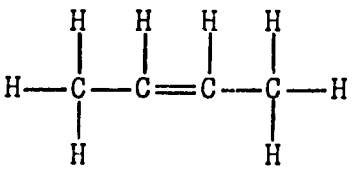
Some of the Higher Homologues



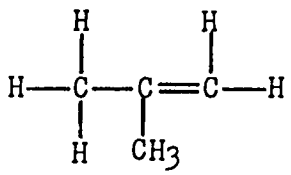
Propylene or propene



1-Butene or ethyl ethylene



2-Butene or symmetrical dimethyl ethylene



2-methyl-1-propene or unsymmetrical dimethyl ethylene

Note that the above three compounds have the same empirical formula C_4H_8 but their graphic formulas show that they are three distinct compounds.

Acetylene Series - Alkines

The members of this series have one or more triple bonds in the molecule. The first member of this series is acetylene or ethine

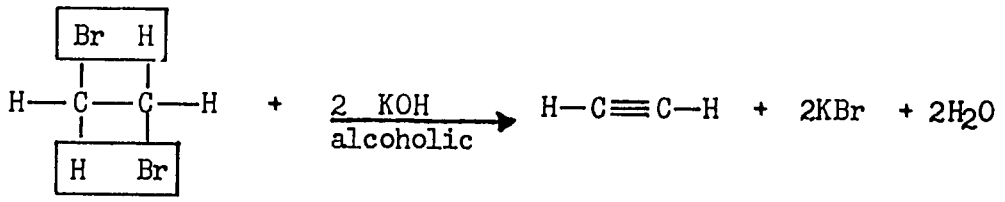
$$H-C\equiv C-H$$

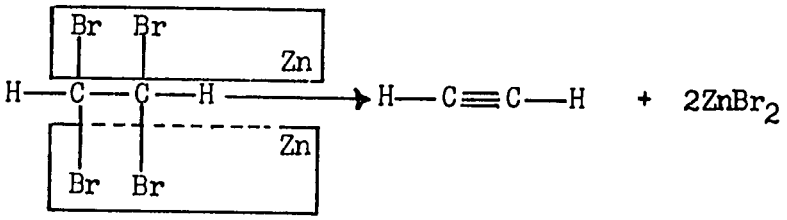
It follows that these compounds are even more reactive than the ethylene series because of the presence of the triple bond.

Preparation

One of the familiar methods of making acetylene is by the action of water on calcium carbide.

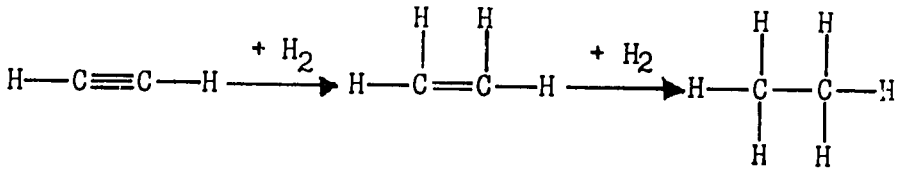
1. $CaC_2 + 2H_2O \longrightarrow H-C\equiv C-H + Ca(OH)_2$

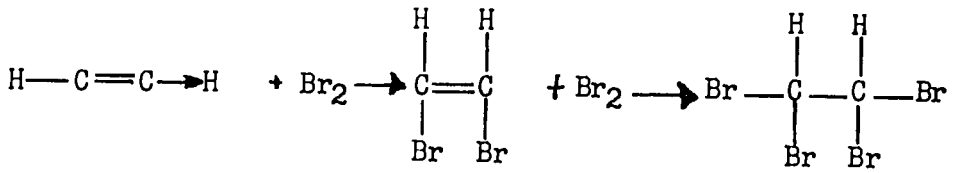
2. 

3. 

Properties

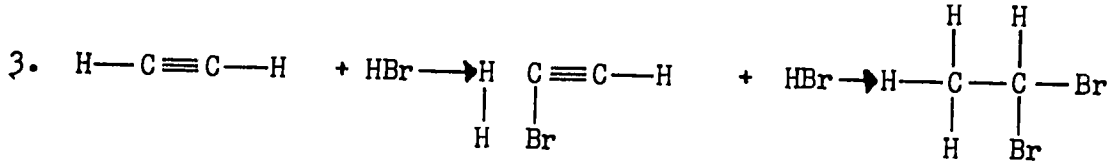
Since acetylene is an unsaturated compound, it will form addition products, but since it is more unsaturated than ethylene it can add to itself more atoms.

1. 

2. 

Acetylene dibromide or dibromoethylene

Acetylene tetrabromide or tetrabromoethane

3. 

Bromoethylene Ethylidene Bromide

ORGANIC CHEMISTRY

LECTURE 13

ALCOHOLS

Alcohols

The alcohols are a very important class of compounds to the organic chemist. They are also very important to the industrial and economic life of our country. They are a very critical group of materials in time of war. In the last decade many uses have been found for them. They are very important intermediates in one process of making synthetic rubber and they also make an excellent fuel for internal combustion engines.

The alcohols may be considered as hydrocarbons in which one or more of the hydrogens are replaced by OH groups. They may also be regarded as derived from water in which one of the hydrogens is replaced by R; H-OH ROH

The relationship of the hydrocarbons to the alcohols is easily shown.

CH_3H	(methane)	CH_3OH	(methanol or methyl alcohol)
C_2H_5H	(ethane)	C_2H_5OH	(ethyl alcohol)
C_3H_7H	(propane)	C_3H_7OH	(Propyl alcohol)
RH	(alkane)	ROH	(alkyl alcohol)

Nomenclature of Alcohols

There are several methods of naming alcohols. The two most important are:

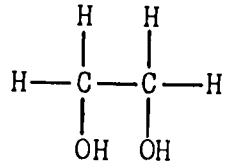
1. The ending e of the hydrocarbon containing the same number of carbon atoms is changed to the ending ol: viz

   C_2H_6 ethane - C_2H_5OH ethanol
   C_3H_6 propene - C_3H_5OH propenol

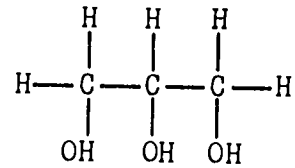
2. The alcohol is named according to the alkyl group it contains:

   C_2H_5H ethane - C_2H_5 ethyl group - C_2H_5OH ethyl alcohol

Alcohols may contain more than one OH group provided they are attached to different carbon atoms; viz

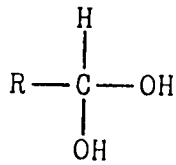


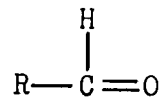
1, 2- ethanediol
or
1, 2- dihydroxyethane
or
glycol



1, 2, 3- propanetriol
or
1, 2, 3- trihydroxypropane
or
glycerol

Two or more OH groups attached to the same carbon atom give rise, as a rule, to unstable compounds.





an aldehyde

An alcohol with one OH group is monatomic; with two OH groups, diatomic; with three, triatomic, etc.

Nature of OH or Alcohol Group

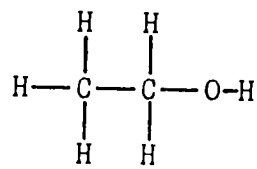
If we take ethyl alcohol and treat it with sodium (Na), only one atom of hydrogen out of the six present is liberated:

$$C_2H_6O + Na \qquad C_2H_5O\ Na + H$$

Thus, it appears that this atom of hydrogen is in a different position in the molecule than the other five. Also, when we treat alcohol with hydrogen iodide, one atom of iodine replaces one atom of hydrogen and one atom of oxygen - that is, it replaces the hydroxyl group.

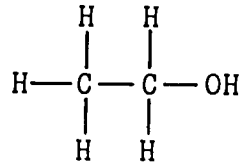
$$C_2H_5OH + HI \qquad C_2H_5I + HOH$$

Thus, we see that one of the hydrogens in ethyl alcohol is attached, not to the carbon atoms, but to the oxygen atom:

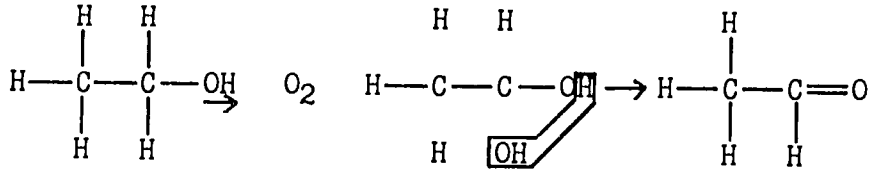


Types of Alcohols

1. Primary alcohol

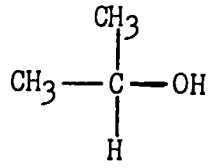
viz 

The alcohol or OH group is attached to an end carbon atom which in turn is attached to one or more carbon atoms and has also two hydrogen atoms. It oxidizes to an acid:



ethyl alcohol — unstable intermediate — acetaldehyde

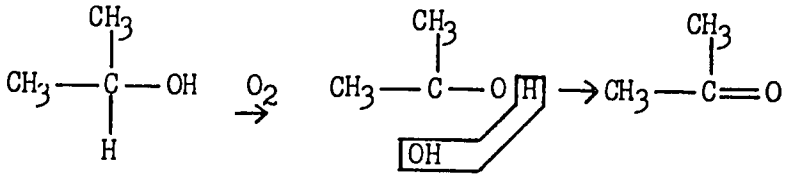
2. Secondary Alcohol



isopropyl alcohol

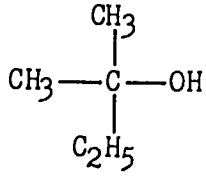
The alcohol group is attached to a carbon atom which has only one hydrogen atom.

It oxidizes to a ketone



isopropyl alcohol — unstable intermediate — acetone

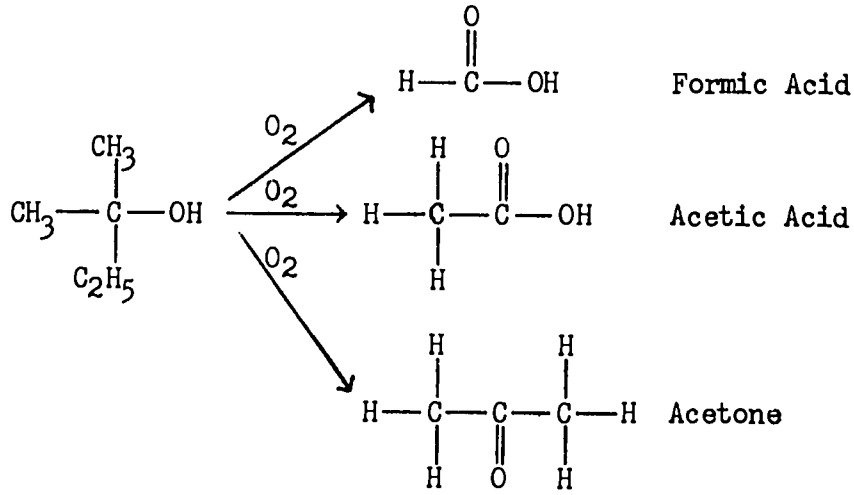
3. Tertiary Alcohol



dimethyl ethyl carbinol

The alcohol group is attached to a carbon atom all of whose other bonds are attached to other carbon atoms.

It is not readily oxidized, but with sufficiently strong agents there is clearage of the carbon to carbon linkages.



Plus CO_2 and HOH

Methods of Preparation

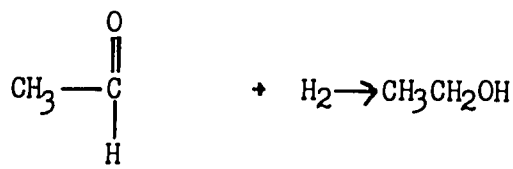
1. Distillation of fermented grains.

2. Action of moist silver oxide or aqueous NaOH on an alkyl halogen compound.

$$C_2H_5\,I + Ag\,OH \longrightarrow C_2H_5OH + AgI$$

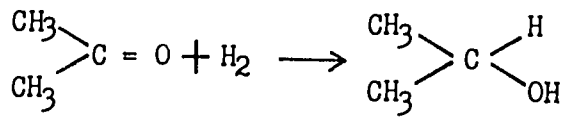
$$CH_3\,Br + Na\,OH \longrightarrow CH_3OH + NaBr$$

3. The reduction of aldehydes to yield primary alcohols.



acetaldehyde

The reduction of ketones to yield secondary alcohols.



4. The action of nitrous acid on a primary amine

$$C_2H_5NH_2 + HONO \longrightarrow C_2H_5OH + N_2 + H_2O$$

5. The hydrolysis of esters

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5 + HOH \longrightarrow CH_3COOH + C_2H_5OH$$

ethyl acetate — acetic acid — ethyl alcohol

Chemical Properties

The alcohols, like water (which they resemble in many ways), are neither acid nor alkaline in reaction.

1. Sodium reacts with alcohol as it does with water, only less violently.

$$2\ C_2H_5OH + 2Na \longrightarrow 2\ C_2H_5O\ Na + H_2$$

sodium ethylate
or
sodium alcoholate

2. As we have already seen, the alcohols oxidize to aldehydes, acids or ketones, depending on the location of the OH group.

3. The OH group can be replaced by a halogen

$$ROH + Hx \longrightarrow Rx + H_2O$$

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

4. Alcohols combine with acids to form esters

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O\boxed{H + HO}\ C_2H_5 \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + H_2O$$

acetic acid — ethyl acetate

Ethers

Ethers may be considered as derived from alcohols in which the H of the ROH is replaced by an R group. As they may be looked upon as derived from HOH in which both hydrogens are replaced by R groups. The ethers are really organic oxides.

Types of Ethers

1. If the two R's represent the same groups, then we get a simple ether

viz. CH_3-O-CH_3 methyl ether

$C_2H_5-O-C_2H_5$ ethyl ether.

2. If the two R's represent different groups, we get a mixed ether

$CH_3—O—C_2H_5$ ethyl methyl ether

$C_2H_5—O—C_3H_7$ ethyl propyl ether

General Methods of Preparation

1. The action of an alkyl halide on sodium alcoholate

$$C_2H_5ONa + I\ C_3H_7 \longrightarrow C_2H_5—O—C_3H_7 + NaI$$

sodium ethylate propyliodide ethyl propyl ether

This is known as the Williamson method.

2. Heating a mixture of silver oxide and alkyl halide

$$2\ C_2H_5I + Ag_2O \longrightarrow (C_2H_5)_2O + 2AgI$$

ethyl iodide ethyl oxide or ethyl ether or ether

This reaction proves that ether is an oxide.

General Properties

The ethers of low molecular weight are colorless, neutral liquids, more volatile than the corresponding alcohols and lighter than water. They are very stable and inactive and are, therefore, used as solvents. The ethers, especially the lower members, are highly inflammable.

Sodium, ammonia, alkalies and dilute acids have no action on them. Hydriodic acid acts in one of two ways.

$$ROR + HI \longrightarrow ROH + RI$$
$$ROR + 2HI \longrightarrow 2RI + H_2O$$

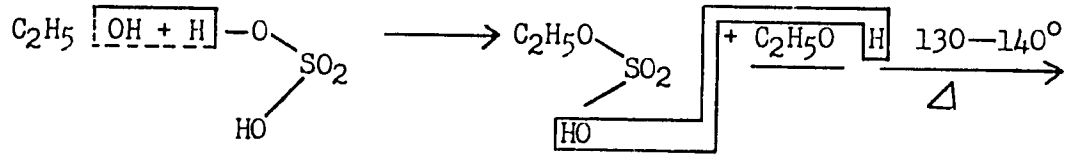
Phosphorus pentachloride when heated acts as follows:

$$ROR + PCl_5 \longrightarrow 2RCl + POCl_3$$

Steam at 150°C decomposes them.

$$ROR + H_2O \longrightarrow 2ROH$$

Chlorine replaces the hydrogens in the alkyl groups. Ethyl ether, famous for its anesthetic properties, is prepared by dehydration of ethyl alcohol with sulfuric acid.



$(C_2H_5)_2O$

usually written $C_2H_5\ \boxed{OH + H}\ O\ C_2H_5 \xrightarrow{H_2SO_4} C_2H_5\ O\ C_2H_5 + H_2O$

Halogen Derivatives of Hydrocarbons

An alkyl halide (or monohalogen derivative of a hydrocarbon) may be regarded as a saturated hydrocarbon in which one of the hydrocarbons is replaced by a halogen (F, Cl, Br or I). Rx is the type formula for an alkyl halide.

General Methods of Preparation

1. The action of a halogen acid on an alcohol in the presence of a dehydrating agent:

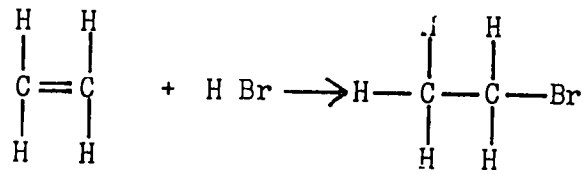
   $C_2H_5\ \boxed{OH + H}\ Br \longrightarrow C_2H_5\ Br + H_2O$

2. By the action of a phosphorus halogen compound on an alcohol:

   $C_3H_7OH + PCl_5 \longrightarrow C_3H_7Cl + POCl_3 + HCl$

   Propyl alcohol Propyl chloride

3. By the addition of halogen acids to unsaturated compounds:



Properties

1. $2\ C_2H_5I + 2\ Na \longrightarrow C_2H_5\ \ C_2H_5 + 2\ NaI$

   ethyl iodide butane

   This is the Wurtz Synthesis.

2. $C_2H_5I + Mg \longrightarrow Mg\begin{cases} C_2H_5 \\ I \end{cases}$

   magnesium ethyl iodide (an intermediate)

This could then be coupled with, say, a ketone to finally yield a tertiary alcohol.

3. $C_2H_5I + KCN \longrightarrow C_2H_5CN + KI$

ethyl cyanide

4. $C_2H_5I + KOH\ (aqueous) \longrightarrow C_2H_5OH + KI$

5. $C_2H_5I + AgNO_2 \longrightarrow C_2H_5NO_2 + AgI$

nitroethane

6. $C_2H_5I + NaOC_2H_5 \longrightarrow C_2H_5OC_2H_5 + NaI$

ethyl ether

7. $C_2H_5I + NH_3 \longrightarrow C_2H_5\,N(H)_3\,I$

ethyl ammonium iodide

8. $C_2H_5I + HOH \longrightarrow C_2H_5OH + HI$

9. $C_2H_5I + \text{Alcoholic KOH} \longrightarrow C_2H_4 + KI + H_2O$

ethylene

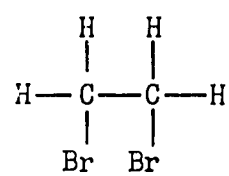
Well Known Members of the Series

Methyl chloride, CH_3Cl, and ethyl chloride, C_2H_5Cl, are used as local anesthetics. When sprayed on the skin the liquids evaporate rapidly, thereby cooling the tissue. To some extent they are also used for refrigerating purposes.

Dihalogen Derivatives of the Paraffins

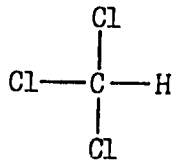
They are usually prepared by the addition of a halogen to an unsaturated hydrocarbon:

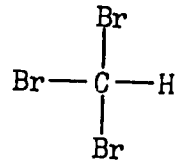
$C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$ or

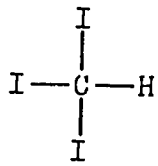


Trihalogen Derivatives of the Paraffins

The important compounds of this type are:

chloroform, 

bromoform, 

and iodoform, 

ORGANIC CHEMISTRY

LECTURE 14

ALDEHYDES, KETONES, ACIDS, ESTERS

Aldehydes and Ketones

An aldehyde $R-\overset{\overset{\displaystyle O}{\|}}{C}-H$, may be regarded as a hydrocarbon wherein a hydrogen atom has been replaced by the $-\overset{\overset{\displaystyle O}{\|}}{C}-H$ group.

A ketone $\begin{matrix} R \\ R \end{matrix}\!\!>C=O$ may be regarded as an aldehyde in which the H of the $-\overset{\overset{\displaystyle O}{\|}}{C}-H$ group is replaced by R; and, on the other hand, an aldehyde may be regarded as a ketone in which one of the R groups is replaced by H. Both have the $>C=O$ or carbonyl grouping. For this reason both aldehydes and ketones have a number of common properties and may be considered together The double bond both in the aldehydes and ketones indicates reactive substances.

Nomenclature of Aldehydes

1. Change the e ending of the hydrocarbon having the same number of carbon atoms (or the ol ending of the alcohol) to al

   viz C_2H_6, ethane - C_2H_5OH, ethanol - CH_3CHO, ethanal.

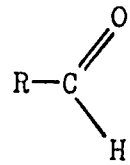
2. The aldehydes may also be named after the corresponding acids formed when the aldehydes are oxidized.

$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ formic acid $\longleftrightarrow$ $H-\overset{\overset{\displaystyle H}{|}}{C}=O$

Formic aldehyde or formaldehyde

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ acetic acid $\longleftrightarrow$ $CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O$

Acetic aldehyde or acetaldehyde

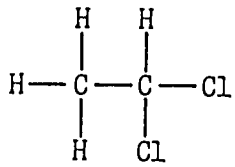
In alcohols the linking is R—O—H and in aldehydes 

When an aldehyde is treated with PCl_5, the reaction is quite different from that obtained when PCl_5 acts on an alcohol. viz using acetaldehyde

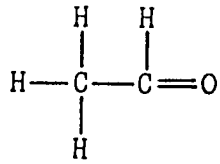
$$C_2H_4O + PCl_5 \longrightarrow C_2H_4Cl_2 + POCl_3$$

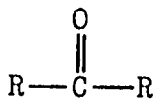
dichloroethane

An examination of the dichloroethane reveals that it is the unsymmetrical variety, the two chlorine atoms being attached to the same carbon atom.



This suggests that the oxygen atom in an aldehyde occupies a position in the chain corresponding to these two chlorine atoms; that is,



<u>Nomenclature of Ketones</u>, 

1. Change the <u>e</u> ending of the hydrocarbon with the same number of carbon atoms to <u>one</u>:

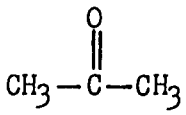
C_3H_8, propane - $CH_3.\overset{\overset{O}{\|}}{C}.CH_3$, propanone

C_4H_{10}, butane - $CH_3.CH_2.\overset{\overset{O}{\|}}{C}-CH_3$, butanone

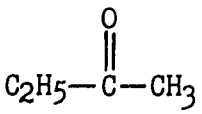
C_5H_{12}, pentane - $CH_3.\overset{\overset{O}{\|}}{C}.CH_2CH_2CH_3$, 2-pentanone

$CH_3.CH_2.\overset{\overset{O}{\|}}{C}.CH_2CH_3$, 3-pentanone

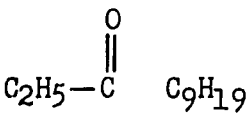
2. Name the compound in accordance with the type of group represented by R, remembering that C = O is the ketonic grouping:



dimethylketone



ethyl methyl ketone

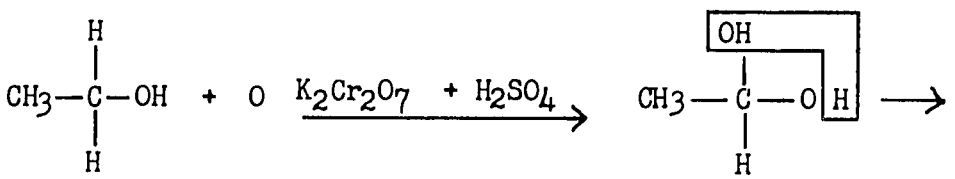


ethyl nonyl ketone

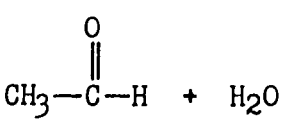
As with ethers we can have simple ketones (dimethyl ketone) or mixed ketones (ethyl methyl ketone).

Preparation of Aldehydes and Ketones

The oxidation of a primary alcohol yields an aldehyde

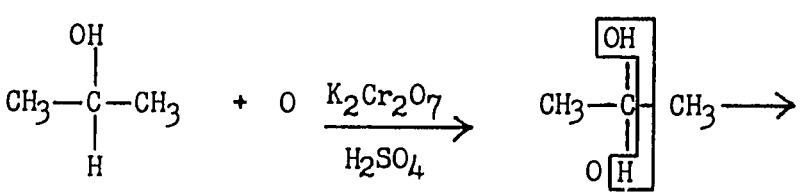


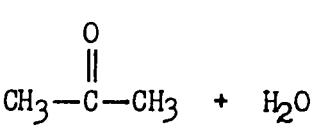
ethyl alcohol



acetaldehyde

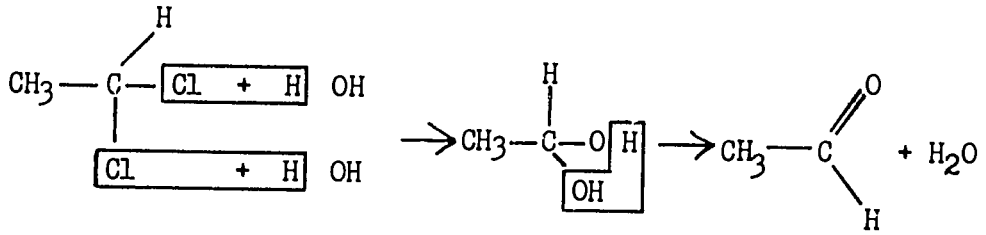
The oxidation of a secondary alcohol yields a ketone



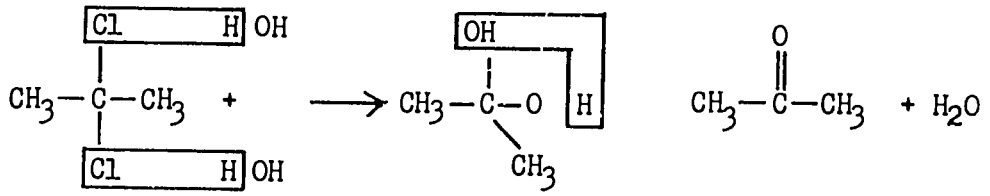


acetone

Hydrolysis of dihalogenated hydrocarbons;



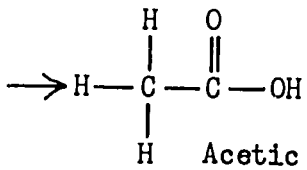
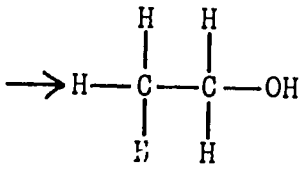
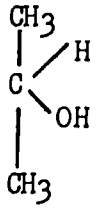
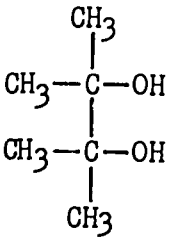
ethylidene chloride + 2 HCl acetaldehyde

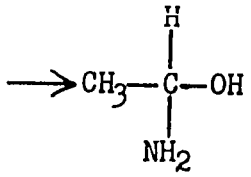
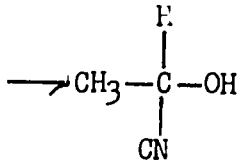
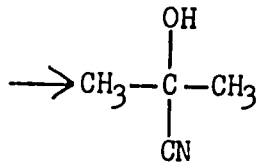
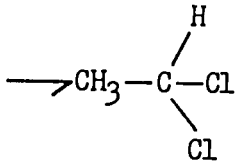
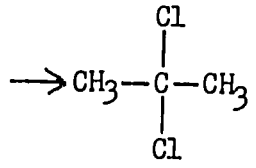
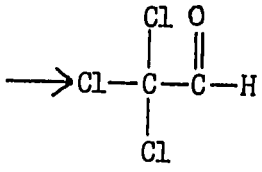
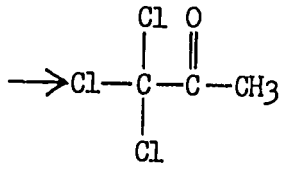
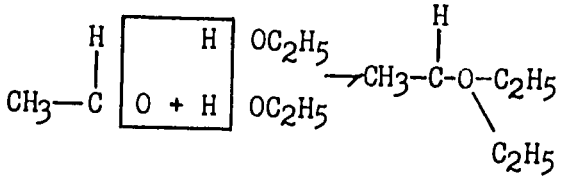


2, 2 dichloropropane + 2 HCl acetone

Chemical Properties of Aldehydes and Ketones

As both aldehydes and ketones contain the carbonyl group, they have many properties in common. Moreover the $>C = O$ group may be looked upon as an unsaturated group, for it contains a double bond, which means that certain types of addition compounds are possible.

Reagents used	Aldehydes e.g. CH_3CHO	Ketones e.g. $CH_3.\overset{O}{\overset{\|\|}{C}}.CH_3$
Oxidation	 Acetic acid	Decomposition of molecule producing acids with lower carbon content as H-COOH and CH_3COOH and $CO_2 + H_2O$
Reduction (H_2)	 ethanol (a primary alcohol)	 a secondary alcohol +  a pinacol (tetramethyl glycol)

Reagents used	Aldehydes e.g. CH_3CHO	Ketones e.g. $CH.\overset{O}{\overset{\|\|}{C}}.CH_3$
NH_3 (ammonia)	 acetaldehyde ammonia	Complex condensation products in place of an addition compound are found.
HCN Hydrogen Cyanide	 acetaldehyde hydrogen cyanide or ethylidene cyanohydrin	 acetone hydrogen cyanide
PCl_5	 ethylidene chloride	 2, 2 dichloropropane
	substitute in CH_3 group	Substitute in CH_3 group
Halogens viz Cl_2	 trichloroacetaldehyde	 trichloroacetone
C_2H_5OH (in presence of a dehydrating agent such as HCl gas)	 acetal	No similar reaction
	Aldehydes reduce ammoniacal silver nitrate solution to produce silver mirror	Ketones do not

Organic Acids

Organic acids contain the carboxyl group $-R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$, and may be regarded as a hydrocarbon in which one or more of the hydrogens is replaced by COOH groups. For instance;

$$CH_3H \longrightarrow CH_3COOH$$

methane acetic acid

If the compound contains one COOH group, it is known as a monobasic acid; if two such groups, dibasic; if three such groups, tribasic. We have analogous types in inorganic chemistry; e.g., HCl - H_2SO_4 - H_3PO_4, etc.

Several acids have names that suggest their origin (formic from "formica", butyric from "butter", valeric from "valeriana", palmitic from "palm oil", etc.) The acids may also be named from their hydrocarbon derivatives by changing the ending e of the hydrocarbons containing the same number of carbon atoms, to oic; so that

CH_4	methane becomes HCOOH, methanoic acid
C_2H_6	ethane becomes CH_3COOH, ethanoic acid
C_3H_8	propane becomes CH_3CH_2COOH propanoic acid
C_4H_{10}	butane becomes $CH_3CH_2CH_2COOH$ butanoic acid

Monobasic Acids (Fatty acid series) RCOOH

The fatty acids are so called because many of them are contained in fats, or are formed from fats on hydrolysis.

General Methods of Preparation

1. Oxidation of a primary alcohol, or of an aldehyde

$$CH_3CH_2OH \xrightarrow{O} CH_3CHO \xrightarrow{O} CH_3COOH$$

2. Hydrolysis of esters (in presence of acids or alkalies)

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5 + HOH \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH + C_2H_5OH$$

ethyl acetate acetic acid ethyl alcohol

3. Hydrolysis of acyl halides with water

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-Cl + HOH \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH + HCl$$

acetyl chloride acetic acid

4. Hydrolysis of alkyl cyanides or of acid amides

$-C\equiv N$ group hydrolyzes to a $-COOH$ group

$$CH_3C\equiv N \xrightarrow{HOH} CH_3-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{HOH} CH_3-\overset{\overset{O}{\|}}{C}-ONH_2H_2$$

methyl cyanide acetamide ammonium acetate

$$\xrightarrow{H_2SO_4} CH_3-C\begin{matrix}\diagup O \\ \diagdown OH\end{matrix} + NH_4HSO_4$$

acetic acid

5. Decomposition of salts of organic acids with mineral acids

$$CH_3.COONa + H_2SO_4 \longrightarrow CH_3COOH + NaHSO_4$$

Sodium Acetate Acetic Acid

General Properties

The lower members up to $C_9H_{19}.COOH$ are liquids with strong odors, and the higher ones waxy solids. They ionize to a slight extent (e.g., $CH_3COO^- + H^+$) but their salts ionize quite considerably. They are stable substances and difficult to oxidize. The acids form:

a.) Salts with bases;

$$CH_3COO\ \boxed{H + HO}\ Na \longrightarrow CH_3.COONa + H_2O$$

sodium acetate

b.) Esters with alcohols;

$$H.COO\ \boxed{H + HO}\ C_2H_5 \longrightarrow HCOOC_2H_5 + H_2O$$

Ethyl formate

c.) Acyl Halides with PCl_5;

$$C_2H_5COOH + PCl_5 \longrightarrow C_2H_5-\overset{\overset{O}{\|}}{C}-Cl + POCl_3 + HCl$$

propionic acid propionylchloride

d.) Halogens substitute in the alkyl group;

$$CH_3COOH + Cl_2 \longrightarrow \underset{\underset{Cl}{|}}{CH_2}COOH + HCl$$

Chloroacetic Acid

Esters

An ester is either an inorganic or organic acid in which the acid hydrogen has been replaced by an R group (or a salt in which the metal is replaced by an R group), viz

CH_3COOH acid, CH_3COOR ester

Esters are widely distributed in nature and are responsible for the characteristic and pleasant odors. They do not ionize and usually are insoluble in water.

General Methods of Preparation

1. By the interaction of an alcohol and an acid: viz

$$C_3H_7\boxed{OH + H}I \longrightarrow C_3H_5I + H_2O$$

$$C_3H_7\boxed{OH + H}HSO_4 \longrightarrow C_3H_7HSO_4 + H_2O$$

propyl hydrogen sulfate

$$C_3H_7O\boxed{H + HO}OC - CH_3 \longrightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}-O-C_2H_5 + H_2O$$

propyl acetate

2. By the interaction of a salt of an acid with an organic halide; viz

$$CH_3COOAg + IC_3H_7 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-O-C_3H_7 + AgI$$

propyl acetate

3. The action of an acyl halide on an alcohol or an alcoholate; viz

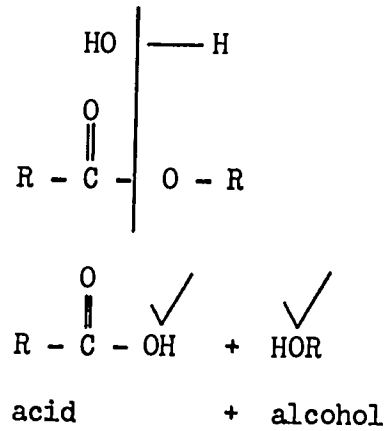
$$C_2H_5O\boxed{Na + Cl}OC.CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + NaCl$$

acetyl chloride ethyl acetate

General Properties

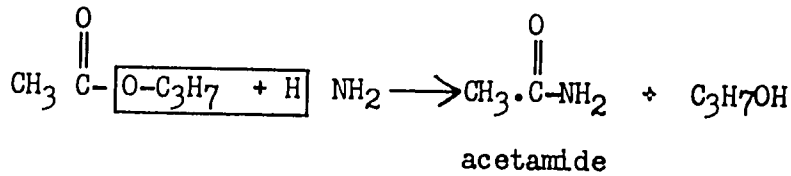
If an ester is boiled with a dilute mineral acid or with a dilute alkali the ester bond is broken at the ether link

viz

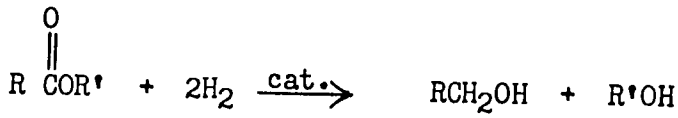


Note that an ester contains both the carbonyl group $\overset{O}{\overset{\|}{C}}$ and an ether linkage $\overset{O}{\overset{\|}{C}}$-O-C- Actually in hydrolysis the acid or alkali merely activates the reaction, for when the bond is broken HOH adds on. The H adds on to the ether type oxygen and the OH group adds on to the carbon atom of the carbonyl group.

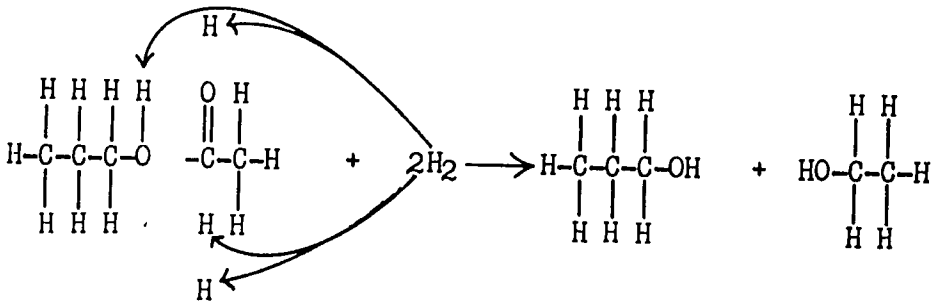
a.) In the presence of ammonia they are converted to the corresponding amide



b.) Hydrogen under pressure and in the presence of a catalyst, the ester is reduced to alcohols.



The mechanism is as follows; using propyl acetate as an example



propyl acetate propyl alcohol ethyl alcohol

The same method of hydrogenation is used, the higher fatty acids to their corresponding alcohols.

viz. $$C_{15}H_{31}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OH + 2H_2 \longrightarrow C_{15}H_{31}CH_2OH + H_2O$$

catyl alcohol

Saponification is the reverse of hydrolysis and may be represented as follows:

$$\overset{\overset{\displaystyle O}{\|}}{RC}\ OH + HOR' \underset{\text{Saponification weak acids or bases}}{\overset{\text{Esterification strong acids}}{\rightleftharpoons}} \overset{\overset{\displaystyle O}{\|}}{RC}\ OR' + H_2O$$

ORGANIC CHEMISTRY

LECTURE 15

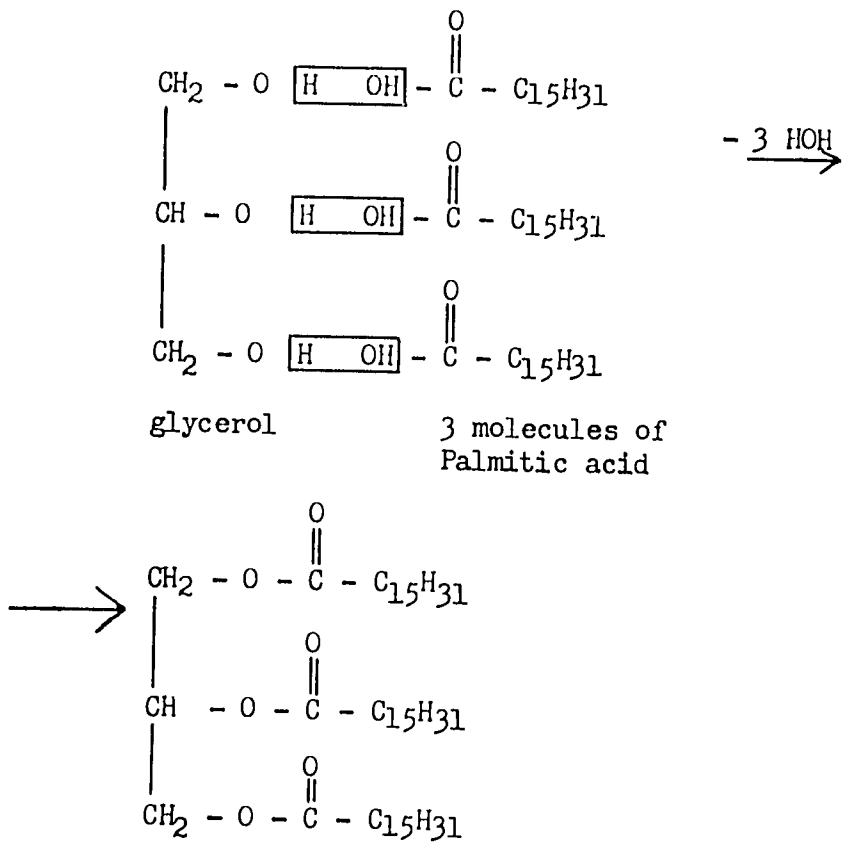
FATS, OILS AND WAXES

Fats are glyceryl esters of high molecular weight fatty acids. You will remember that it is due to the early development of knowledge about these acids derived from fats which led to the classification of straight chain compounds as aliphatic.

It is quite striking that among some fifty acids found in nature, almost all are straight chain acids, containing an even number of carbon atoms. The only odd numbered fatty acid isolated from fats is iso-valeric acid $(CH_3)_2CH\ CH_2COOH$, which occurs in relatively large amounts in the dolphin and porpoise. Saturated fatty acids ranging from C_4 to C_{26} have been identified as constituents of fats. Of these palmitic acid is of widest occurrence. Many of these acids are derived from vegetable sources, others from animal. Stearic acid occurs in large amounts in the fats of animals. (10-30%)

Thus these fatty acids belong to the class of acids which we have already studied having the general formula RCOOH.

These glyceryl esters of the fatty acids are formed when HOH is split off from the carboxyl group of an acid and the OH group of a trihydroxy alcohol, usually glycerine.

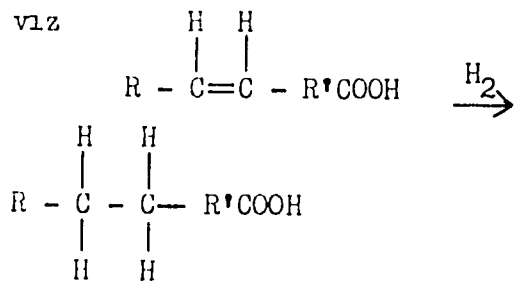


If the three acid radicals are the same, it is known as a simple glyceride. A fat containing radical of two or three different fatty acids is known as a mixed glyceride. The table on page 109 of Lowy and Harrow lists the most important fats and oils, their sources and the acids which are combined as esters with glycerine. Fats and oils have the same general composition, the determining factor of whether the glyceride is a solid or an oil, being the combination of acids combined.

Hydrogenation of Fats

For the manufacture of soap and for use as certain foods, solid fats are preferable to liquid ones, which predominate in nature. Since the melting point depends on the extent of unsaturation, natural fats can be hardened by hydrogenation. (You remember hydrogenation means adding hydrogen to the double bonds existing in these long chain acids.

viz



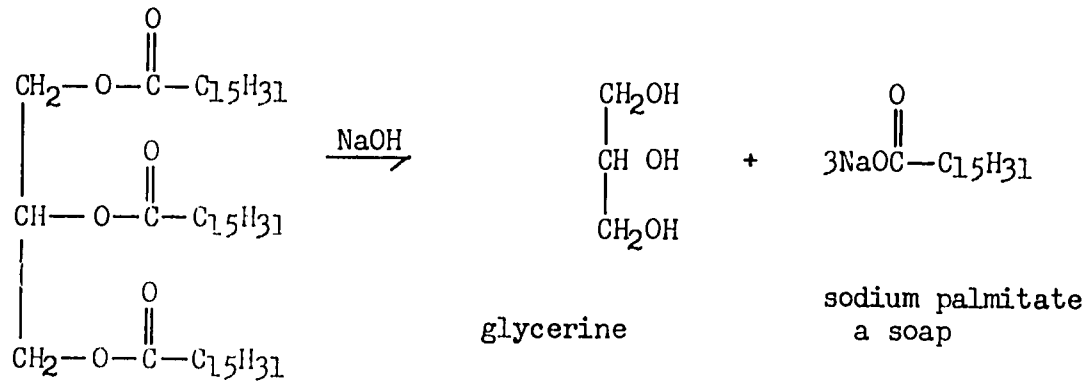
This is the reaction we studied in the alkene series.)

Vegetable oils such as cottonseed, soybean, and peanut are often either partially hardened to the consistency of lard, or completely hardened (hydrogenated) and then mixed with low melting oils. If desired as a butter substitute the product is churned with milk that has been slightly soured to simulate butter flavor. Lard is often partially hydrogenated to improve the the keeping qualities, since the development of rancidity is associated with unsaturation.

Soaps

When a fat is treated with NaOH (sodium hydroxide) the ester is hydrolyzed (remember this reaction as being general for esters as previously noted). This is the general way homemade soaps were made (boil animal fat with lye).

By this means the glycerine is recovered and the sodium salt of the acids is formed. These salts are soaps, viz.



glyceryl palmitate

This is the main constituent of the famous "Palmolive" soap, the remainder being the sodium salt of olive oil.

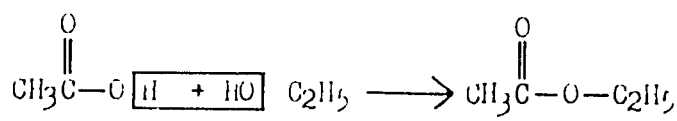
A group of detergents (Gardinol, Dreft, Drene, Modinal) introduced in Germany about 1930 are sulfates of long chain alcohols prepared by the hydrogenation of fats:

$$RCOOH \xrightarrow{H_2} RCH_2OH \xrightarrow{O(SO_2ONa)_2} RCH_2OSO_2ONa$$

The potassium salts of fatty acids are softer and more soluble and serve special purposes, shaving cream, liquid soap, etc.

<u>Waxes</u>

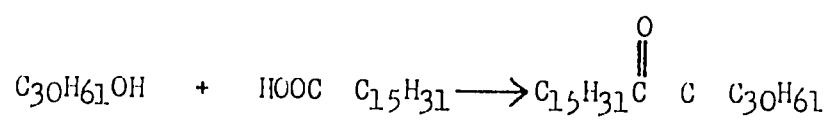
Waxes are esters formed between a fatty acid and a long chain alcohol. This is an ester formed between one molecule of an alcohol and one molecule of a fatty acid. This is the same as:



acetic acid ethanol ethyl acetate (sweet smelling) (good solvent)

Except that in waxes both the acid and the alcohol are long chained and of higher molecular weight.

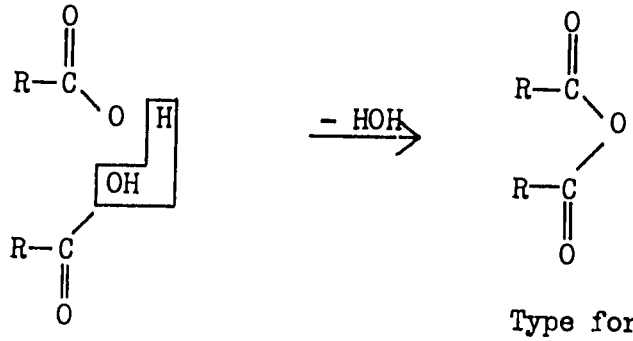
viz



myricyl alcohol palmitic acid myricyl palmitate (in beeswax)

Acid Anhydrides

An acid anhydride is formed when two acids combine to lose HOH viz:



Type formula for anhydride

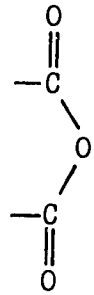
In this type compound there is an ether link between the two carbonyl groups. viz

carbonyl group

—O—

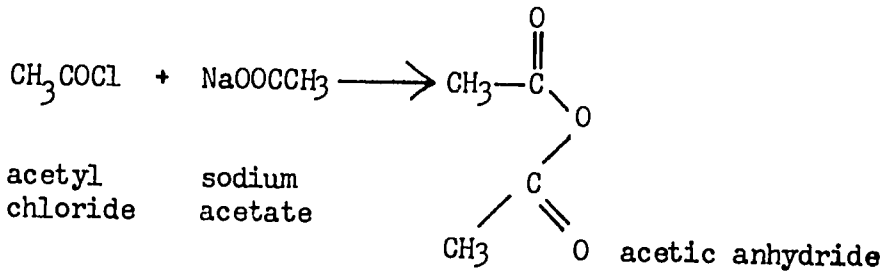
ether link

therefore



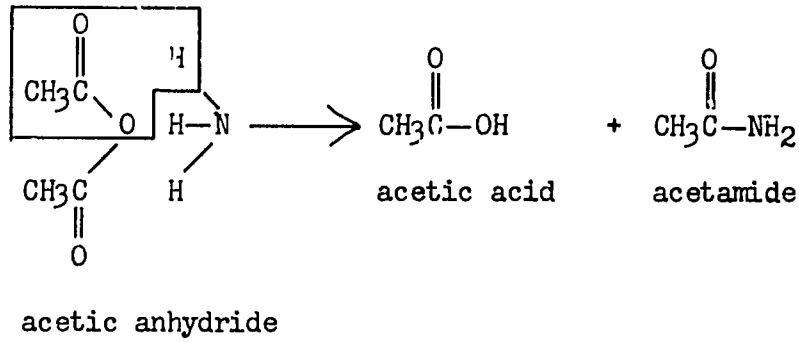
anhydride group

Only the low molecular weight anhydrides are important. They are formed usually by the action of a strong dehydrating agent on the corresponding acid. Also by heating an acyl halide with the salt of the acid. viz



In the presence of water they immediately decompose to the corresponding acid.

In the presence of ammonia an amide and an acid are formed. viz:



<u>Acyl Halides</u>

Type formula $R-\overset{\overset{\displaystyle O}{\|}}{C}-X$

This is an acid in which the OH group of the acid is replaced by a halogen, such as chlorine, viz:

$RC(=O)-$ acyl group

$$\underset{\text{acetic acid}}{CH_3C(=O)-OH} + \underset{\text{phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\text{acetyl chloride}}{CH_3C(=O)-Cl} + POCl_3 + HCl$$

These compounds are very reactive and the halogen is readily split off, thus freeing the acyl group to react with any other free group.

Thus, with sodium acetate it forms acetic anhydride.

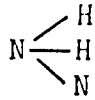
$$CH_3C(=O)-\boxed{Cl + Na}\ OOCCH_3 \longrightarrow \underset{\text{acetic anhydride}}{CH_3C(=O)-O-C(=O)-CH_3} + NaCl$$

and with alcohol to form an ester

$$\underset{\text{acetyl chloride}}{CH_3C(=O)}\ \boxed{Cl + H}\ \underset{\text{ethanol}}{OC_2H_5} \longrightarrow \underset{\text{ethyl acetate}}{CH_3C(=O)-OC_2H_5}$$

<u>Acid Amides</u>

Type formula $R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

Again we have compound derived from an acid in which the OH group is replaced by the $\underline{NH_2}$ group. Or we might say that one of the hydrogens of ammonia  is replaced by the acyl group which we just considered.

However, the combination of the acyl group with NH_2 forms a new group of compounds called amides.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

We will soon learn that the NH_2 group is the amine group and thus in an amide we have both the carbonyl group $\overset{\overset{\displaystyle O}{\|}}{\underline{C}}$ and the NH_2 group (amine) combined to a hydrocarbon radical. viz

$$\underset{\text{methyl group}}{CH_3-} + \overset{\overset{\displaystyle O}{\|}}{C} + NH_2 \longrightarrow \underset{\text{acetamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-N\begin{matrix}H\\H\end{matrix}}$$

These compounds are of considerable interest to the chemist and the biochemist and we have already seen how they may be prepared from an acyl halide or an anhydride by the action of ammonia.

However, because of the limited scope of our work we will merely give them a passing mention and go on to the consideration of compounds which will more closely fit our integrated plan of study.

Substituted Acids

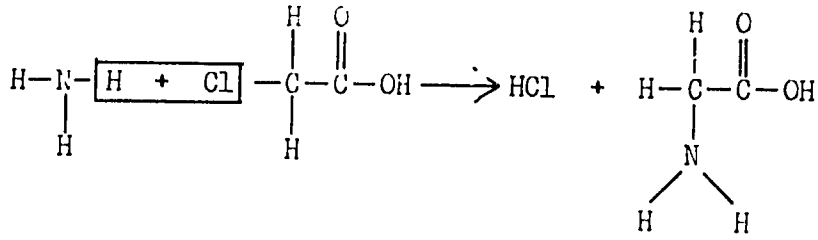
We should by now easily recognize the type formula for an acid $R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ and we know that this is usually considered to be an alkyl radical R (such as CH_3^-, methyl; C_2H_5-, ethyl; etc.) combined with the carboxyl group COOH or $\overset{\overset{\displaystyle O}{\|}}{C}-OH$ which is the special grouping which denotes an organic acid. Moreover we have just finished considering the various reactions of this carboxyl group wherein it forms esters, acyl halides, amides and anhydrides.

However, as I have mentioned before the alkyl portion of the acid may be attached, that is have some of its hydrogens substituted, without affecting the carboxyl group.

For instance, chlorine gas will substitute one or more of the group depending on how much is used and the conditions of catalyst, pressure and temperature. viz

$$\underset{\text{acetic acid}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{chlorine}}{Cl_2} \longrightarrow \underset{\text{mono-chloroacetic acid}}{Cl-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + HCl$$

This acid in turn can be interacted with ammonia to form an amino acid. viz



amino acetic acid
or glycine

Glycine is the first of an important series of compounds called amino acids. We will hear more of these when we come to consider proteins. These amino acids are the "building blocks" of the proteins. The various proteins which we ingest into our systems as food are broken down in the stomach into these various amino acids. These amino acids are then absorbed into the blood stream where they are carried to the various parts of the body to be again combined into different proteins as needed at the different points. It is in this manner that cell tissues are built up; also, the collagen of the skin and the keratin of the epithelial layer and of the hair.

ORGANIC CHEMISTRY

LECTURE 16

AMINES

The amines are the bases of organic chemistry and the type formula is $R\text{-}NH_2$. They may be considered as derived from ammonia NH_3 in which one of the hydrogens is replaced by an alkyl group.

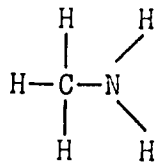
viz CH_3NH_2 or $C_2H_5NH_2$

methyl amine ethyl amine

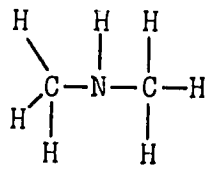
If two of ammonia's hydrogens are replaced by alkyl groups, the compounds formed are known as <u>imino</u> compounds. However, these compounds are not important in relation to the amines and for that reason we will concentrate on the amines.

The amines are classified as primary, secondary or tertiary depending on whether one, two or three of the hydrogens are available.

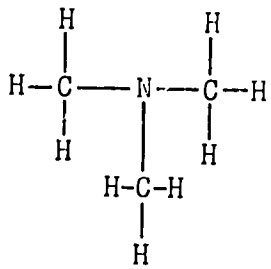
viz



methyl amine



dimethyl amine



trimethyl amine

<u>Method of Preparation of Primary Amines</u>

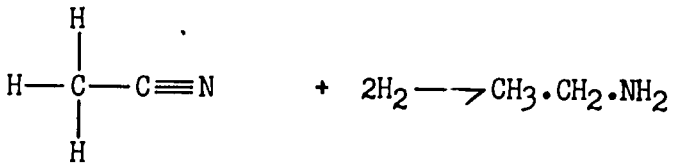
1. The action of bromine and a strong base on an amide.

$$\underset{\text{acetamide}}{CH_3\overset{O}{\overset{\|}{C}}\text{-}NH_2} + Br_2 + NaOH \rightarrow CH_3\overset{O}{\overset{\|}{C}}\text{-}N\begin{matrix}H\\Br\end{matrix} + NaBr + H_2O$$

$$+ 3NaOH \rightarrow \underset{\text{methyl amine}}{CH_3NH_2} + Na_2CO_3 + NaBr + H_2O$$

This is known as the Hoffmann reaction. It is particularly significant for in the course of this reaction we have arrived at a compound which has one carbon atom less than in the original compound. This reaction is often selected for this particular peculiarity. It is known as a degradation.

2. Reduction of alkyl cyanides



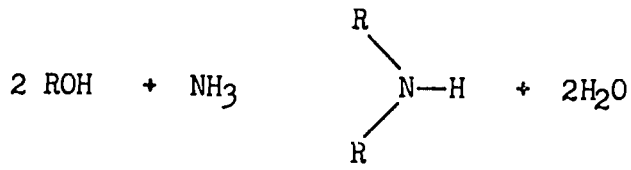
methyl cyanide ethyl amine

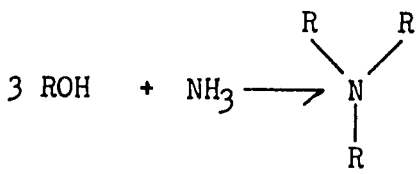
3. By the catalytic dehydration of an alcohol and ammonia.

$$CH_3OH + H\ NH_2 \longrightarrow CH_3NH_2 + H_2O$$

methyl alcohol ammonia methyl amine

By controlling concentrations and changing the conditions, varying amounts of the corresponding secondary and tertiary amines are formed.

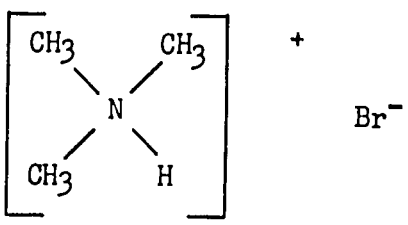




Properties of Primary Amines

These compounds have a strong fish-like odor. They are more basic than ammonia and are soluble in water. They also give an alkaline reaction in water and form salts with acids. These salts formed with acids are due to an increase in the valence of nitrogen from three to five, the fifth linkage being polar in character.

viz: with H Br

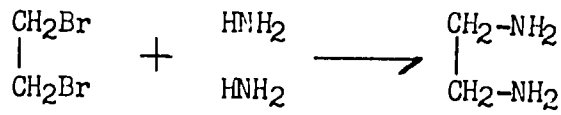


The salts are odorless solids and the amine is readily released by the addition of a strong alkali.

By interaction with nitrous acid we may detect whether an amine is primary, secondary or tertiary.

primary amine & nitrous acid ⟶ alcohol
secondary amine & nitrous acid ⟶ yellow nitroso compound
tertiary amine & nitrous acid ⟶ a salt

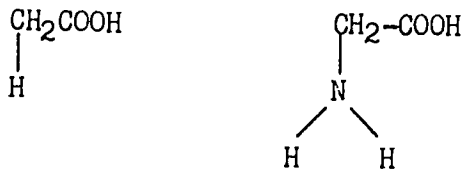
As in the case of alcohols, it is possible to have compounds with two amino groups. viz:



ethylene bromide ammonia ethylene diamine

Amino Acids

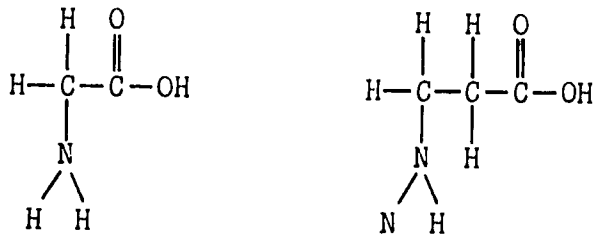
An amino acid is a compound in which one of the hydrogens in one of the carbon atoms adjacent to the carboxyl group is replaced with an amino group. viz:



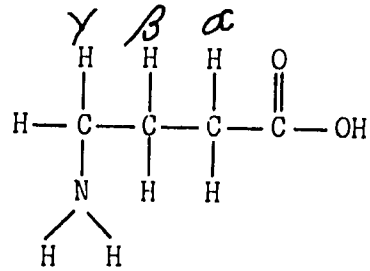
acetic acid amino acetic acid, or glycine

The location of the amino group is determined relative to the carbon atom of the carboxyl group. The distance away is designated by the Greek letters of the alphabet which correspond to our a, b, c, etc.

viz: α β α



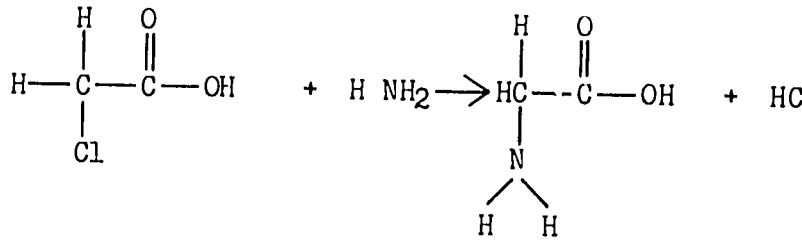
α amino acetic acid β amino propionic acid



γ amino butyric acid

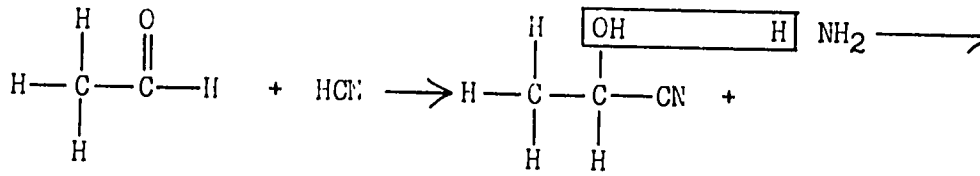
Methods of Preparation

1. The action of ammonia on halogen acids

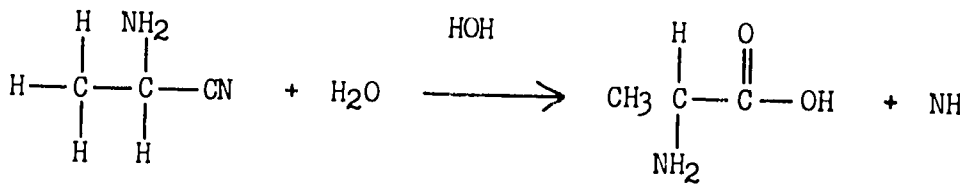


glycine

2. The action of hydrogen cyanide on aldehydes and ketones, and the subsequent reaction with ammonia and hydrolysis.



acetaldehyde hydrogen cyanide



α amino propionic acid

3. The hydrolysis of proteins by enzymes, acids, or alkalies. In this case just amino acids are obtained.

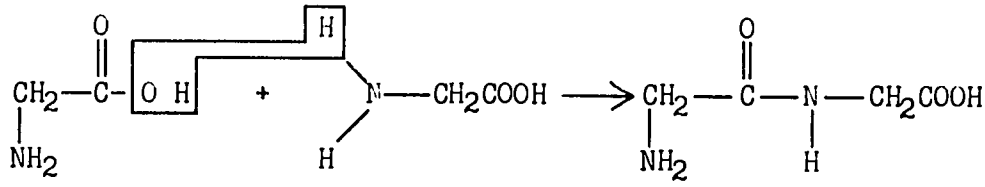
Properties

The amino acids are a particularly interesting group of compounds as within the same molecule both the acid and basic groups of organic chemistry co-exis that is, the carboxyl and the amino groups.

Thus, they may act either as acids or bases depending on the conditions. The amino acids are the compounds, which through our arteries and veins, are

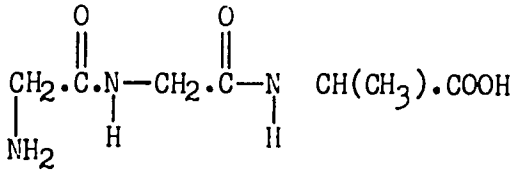
carried to the various portions of our bodies where they are converted into tissues, muscular and collagen fibers, etc. as needed.

It has been quite positively determined that amino acids combine in various combinations or groupings to form proteins. The exact manner in which they combine is not positively known, but it is believed to be through their active carboxyl and amino groups by what is known as the peptide linkage. viz:



glycine glycine glycyl glycine
a dipeptide

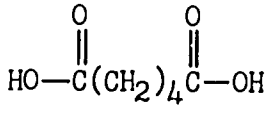
It is possible to combine different amino acids. viz:



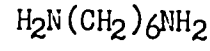
glycyl glycyl alamine - this is a tripeptide

The methods by which these peptide type compounds are made in the laboratory are quite difficult and the yields are low. However, they have aided the chemist in his search for an understanding of protein structure. At the present time it is believed that all proteins are made up of combinations of various amino acids as shown above to give large molecules having molecular wts. of from 50,000 to 300,000.

A good example of a man made polymer containing peptide linkages is <u>polymer 6-6</u>. Its constituents are adipic acid and hexamethylene diamine.

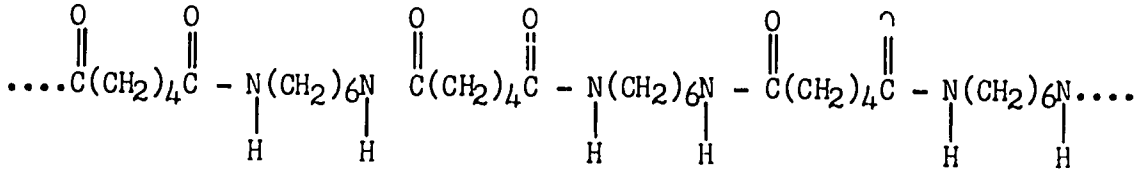


adipic acid



hevamethylene diamine

It polymerizes as follows:



It is removed from autoclave above its melting point (263°C) and extruded through small orifices in an atmosphere of nitrogen (to prevent oxidation) giving threads or fibers. This material is sold under the trade name of nylon.

Proteins

Among the three classes of food stuffs, simple fats, carbohydrates and proteins, the proteins alone contain the element nitrogen, and as a rule sulfur. The average percentage composition of proteins is (C, 53%) (O, 23%) (N, 16%) (H, 7%) and (S, 1%).

The proteins are important constituents of our foodstuffs. It is by the ingestion of proteins into our bodies that we keep our body proteins built up.

We know that all our body tissues, muscles, skin and hair are made up of proteins. The proteins in our bodies are made up of different combinations and total amounts of α amino acids than contained in the proteins of our food. However, the food protein is hydrolyzed in our digestive system to about 22 different α amino acids. In the form of amino acids they are conveyed into the blood stream where they are transported to various portions of the body. Thus at any point where more skin protein or muscle protein, for instance, is needed they recombine in the proper proportions. This part of the process has been definitely determined, but the acting force which enables them to recombine into the proper protein is still unknown.

The various proteins known at the present time have been classified by several systems, none of which is too satisfactory. They have been classified, for instance, by their solubilities, isoelectric points and molecular weights. These classifications contain complicated sub-divisions.

Fortunately for the leather chemists a new classification has been derived which divides the proteins into two main groups: fibrous and globular. The fibrous proteins are the proteins of the skin (collagen), hair (keratin) and elastin. The fibrous proteins are associated with the skeletal structure of the body. They are large molecular weight materials insoluble in neutral solvents or slightly acid or alkaline solutions, but have the property of swelling in acid or alkaline solutions. These proteins are of interest to the tanner.

The globular proteins are non-fibrous in nature and are soluble in the above solvents. Thus, we can readily see that these are the protein molecules which are removed in soaking, liming and bating. There is not enough knowledge yet to show whether their complete removal is desirable or not.

It has been recently believed that the globular proteins may be the building blocks of fibrous proteins. That is, they may be fibrous proteins in the process of being built or proteins stored to replenish fibrous proteins.

ORGANIC CHEMISTRY

LECTURE 17

CARBOHYDRATES

The very name indicates that the members of this group are made up of carbon (C), hydrogen (H) and oxygen (O). It is interesting to note that hydrogen (H) and oxygen (O) are present in the proportion of 2:1; just as in water.

The carbohydrates are in many cases polyhydroxy aldehydes and polyhydroxy ketones, or compounds which may be converted into such aldehydes and ketones.

The carbohydrates are derived mainly from the vegetable kingdom and they represent one of the three great classes of foodstuffs.

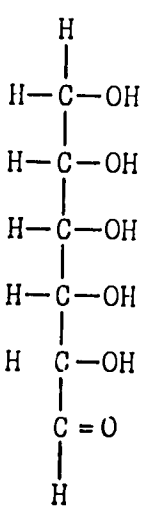
The carbohydrates fall into two main classes:

I. The sugars - sweet, crystalline compounds.
II. The starches and celluloses - tasteless non-crystalline compounds.

The carbohydrates are named according to the number of carbon atoms in the compound as in the case of the monosaccharides.

The most important member of the monosaccharides is the hexoses. The formula for a hexose is $C_2H_{12}O_6$. Glucose, mannose, galactose, fructose and sorbose all have this formula.

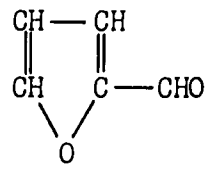
Glucose is present in the juice of many sweet fruits, such as grapes. It is necessary constituent of blood. From its formula we can readily recognize groupings that we have already studied.



It has several hydroxyl groups similar to glycerine (trihydroxy propane) and yet the presence of the $\overset{H}{|}$ group at the end of the molecule shows it to be a member of the aldehyde - C=O family.

As we would expect, the alcohol groups react with acetyl chloride or acetic anhydride just as do the alcohols that we have studied. They also react with hydriodic acid (HI).

Likewise the aldehyde group undergoes reactions with HCN (hydrogen cyanide) and (NH_2OH) hydroxylamine just as do the regular aldehydes. Glucose reacts with Molisch reagent (α naphthol) and concentrated H_2SO_4 (sulfuric acid) to give a violet ring or color. This is said to be due to the formation of furfural:



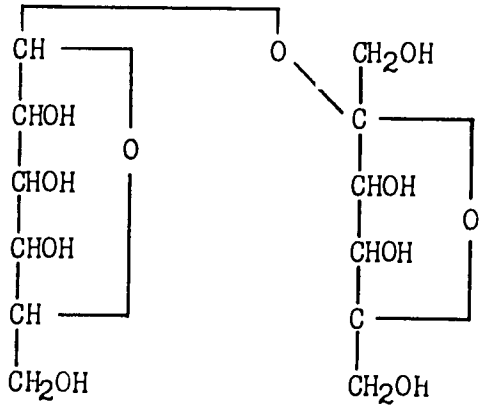
Thus we see a close structural similarity between glucose and furfural. This no doubt explains why the cereal foods are such a good source of furfural.

Glucose is used by the tanner in the preparation of one-bath chrome liquors. The first reference of this use is ascribed to Procter in 1897. Glucose is a cheap material for the reduction of chromic acid in hot, fairly concentrated solutions. Other similar materials such as cane sugar, molasses, glycerin and cellulose extracts may be used. However, the choice depends on the cost factors and also on the undesirability of certain contaminating materials which may be present as impurities.

The sugars, such as glucose, fructose and sucrose when treated with yeast (which contains the enzyme zymase) yield ethyl alcohol and carbon dioxide (CO_2). We have already referred to this common reaction, better known as fermentation.

Sucrose (cane sugar) is classified as a di-saccharide for it is made up of two mono-saccharides condensed together. Two other important disaccharides are lactose (milk sugar) and maltose (malt sugar).

The following is the suggested formula for sucrose:



Glucose part Fructose part

On acid hydrolysis sucrose yields a mixture of glucose and fructose. When sucrose is heated above its melting point caramel is formed. Caramel is extensively used as a coloring material for food preparations. It is also added to alcohol to give a brown color, the purpose being to simulate the color of good whiskey.

Starch ($C_6H_{10}O_5$) is known as a polysaccharide. It is made up of many monosaccharides condensed together; however, we do not know the exact number and designate the regular formula for a monosaccharide taken x times.

Cellulose $(C_6H_{10}O_5)x$ is the chief constituent of the cell wall of plants. Cotton is almost pure cellulose. It has the same general formula as starch and for the same reason. When cellulose is hydrolyzed it yields glucose.

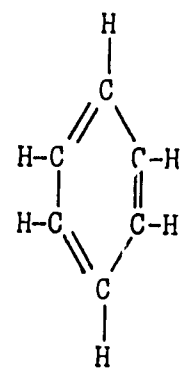
Cellulose is a very important compound to man and the chemist by proper treatment has converted it into rayon (cellulose acetate), photographic film (cellulose nitrate) etc.

Aromatic Hydrocarbons

Up to this point we have been considering various straight chain hydrocarbons and the various groups (alcohols- OH) (amines- NH_2) etc. which when part of the chain form certain distinct classes of compounds.

You will remember that methane (CH_4) was the smallest possible hydrocarbon of the aliphatic series and thus was considered the mother compound of the series. In like manner benzene occupies the same position in the aromatic series.

Benzene has the formula C_6H_6 and extended studies have proved it to have a ring structure:

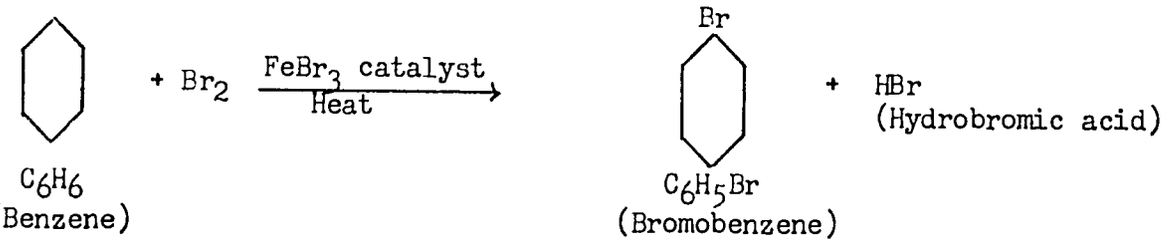


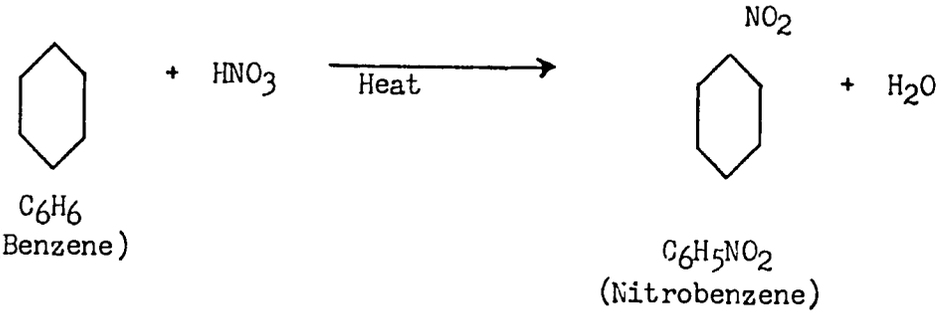
Also, as carbon must maintain its valence of 4, certain unsaturated or double bonds are indicated. There are three of these double bonds equally spaced as indicated above.

Up until now we have seen that an unsaturated bond such as exists in the alkenes is very reactive and addition to the double bond is quite simple and rapid. As a matter of fact, the addition of Br_2 to a double bond type of compound in the aliphatic series is a typical reaction.

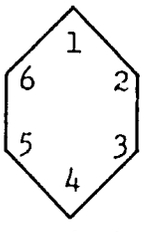
However, in the case of benzene the double bonds are not very reactive and bromine does not add to them. As a matter of fact, none of the other typical additional reactions of alkenes take place. Under forcing conditions (pressure, high temperature and sometimes a catalyst) bromine, sulfuric acid and nitric acid can be caused to react with benezene, but the typical reaction

products are not those resulting from additions, as in the series of olefinic hydrocarbons, but from substitutions, viz.

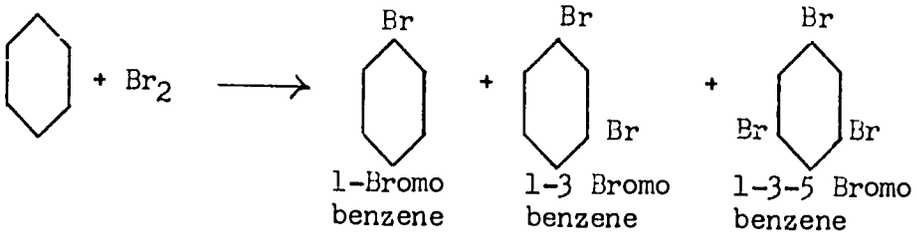




When reactions such as the above take place it is possible to have mono, di or even tri substitution. And these substitutions will follow certain uniform procedures. Thus, if we number the carbons in the ring:

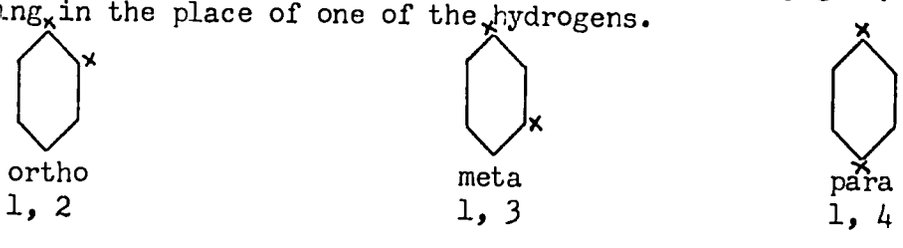


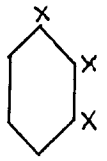
The following substitute products may be formed when a reaction takes place say with bromine:



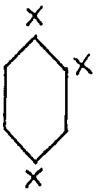
The percentage of these that are formed depends on the conditions of the reaction.

The possibilities for di and tri substitution are as follows, using outline formulas. X in this case merely represents any group which enters the ring in the place of one of the hydrogens.

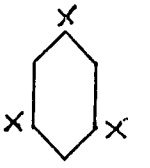




Vicinal
1, 2, 3

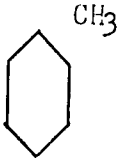


Asymmetrical
1, 2, 4



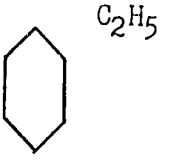
Symmetrical
1, 3, 5

In compounds such as



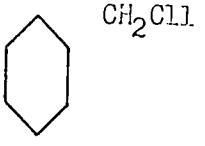
methylbenzene

or

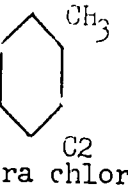


ethylbenzene

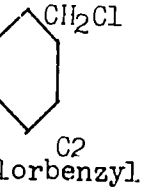
The CH_3 and C_2H_5 groups are spoken of as "side chains". The benzene residue being called the nucleus. Substitution may take place in the side chain, or in the nucleus, or in both, yielding various products:



benzyl chloride



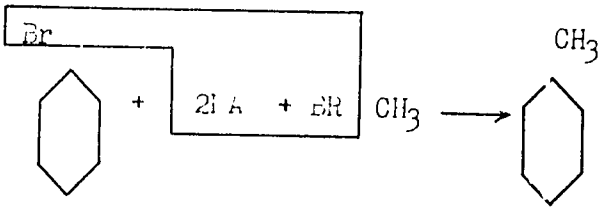
para chlortolvene



para chlorbenzylchloride

General Methods of Preparing Aromatic Hydrocarbons

1. Fitting Synthesis

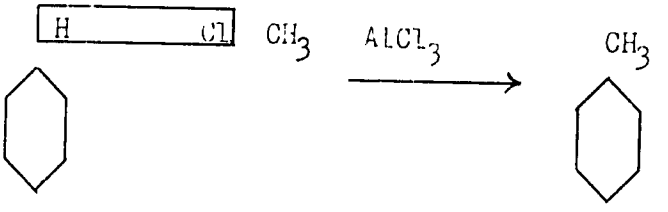


+ 2NaBr

tolvene

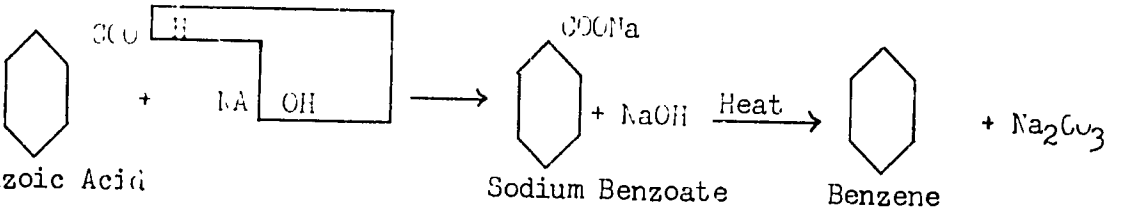
sodium bromide

2. Friedel-Crafts



+ HCl

3. By heating salts of aromatic acids



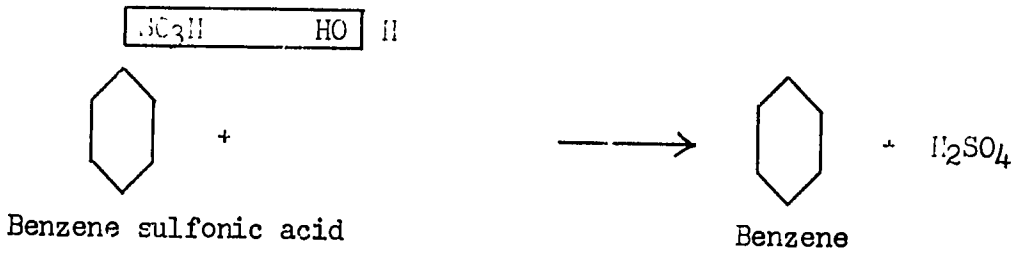
+ Na_2CO_3

Benzoic Acid

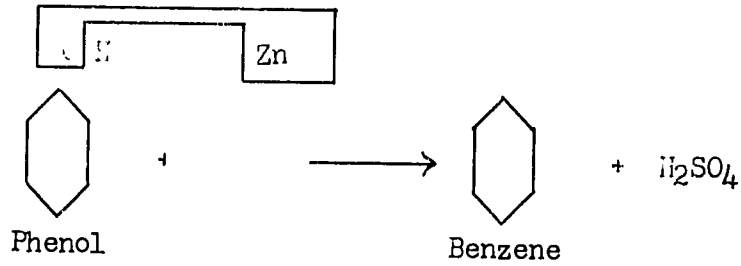
Sodium Benzoate

Benzene

4. By elimination of SO_3H group (use steam + acid)

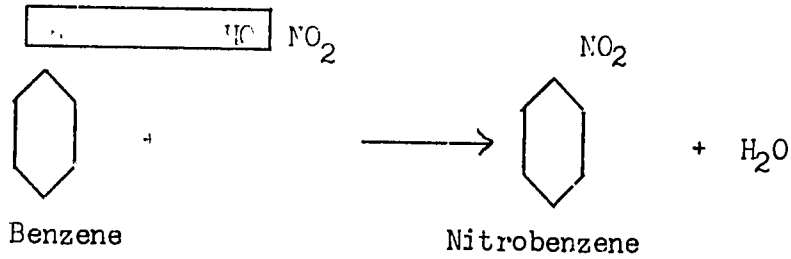


5. By distilling phenol with zinc dust

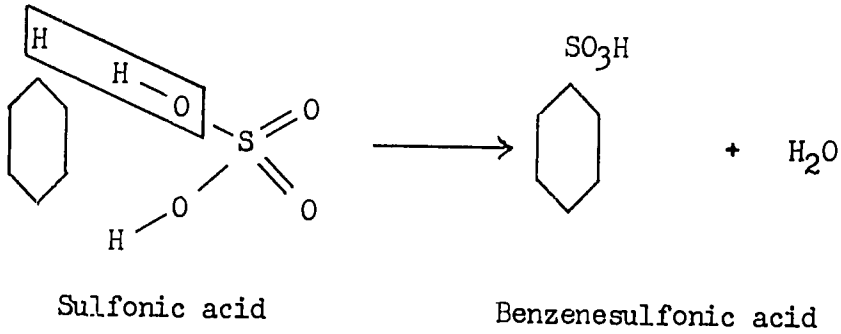


General Reactions of Aromatic Hydrocarbons

1. With intric acid to form nitro compounds

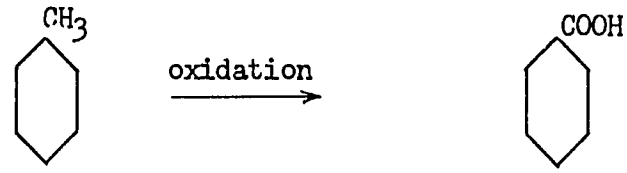


2. Reactions with sulfuric acid to form sulfonic acids



3. Oxidation

A side chain whether CH_3 or any other group containing carbon may be oxidized to the carboxyl group (COOH)



Toluene Benzoic Acid

These three reactions- nitration, sulfonation and oxidation, bring out the essential differences of aromatic and aliphatic hydrocarbons.

ORGANIC CHEMISTRY

LECTURE 18

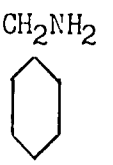
AROMATIC AMINES

We have already seen that three reactions in particular are peculiar to aromatic chemistry. These reactions are sulfonation, nitration and oxidation. The first two reactions, sulfonation and nitration, are particularly important as they are intermediate steps leading to the formation of many important chemicals.

By sulfonation we can make many previously insoluble aromatic compounds soluble. By nitration we take the first step in the formation of amines, dyes, drugs, etc.

As already shown, the $-NH_2$ group is the amino group and it is derived from ammonia by the removal of one of the hydrogens. This amino group can be attached directly to the ring or to a side chain which is itself attached to the ring. The chemical nature of the compound varies considerably, depending on whether the amino group is attached to the ring or not. viz

amino benzene
or aniline

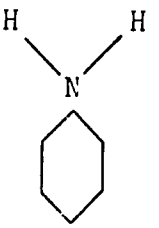


benzylamine

The benzylamine shows the general properties of an aliphatic amine since the $-NH_2$ group is on the side chain. That is, it will undergo the chemical reactions which are peculiar to aliphatic amines in general, the reactions with various other chemicals which we noted when we considered straight chain amino compounds.

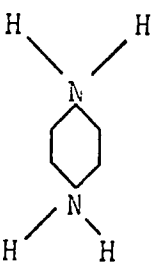
Just as in the case of the aliphatic amines, the aromatic amines may be primary, secondary or tertiary, depending on whether one, two or three of the hydrogens attached to the nitrogen are replaced by other groups.

<u>Primary</u>

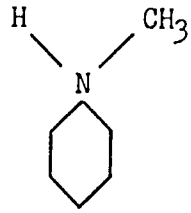


aniline

or

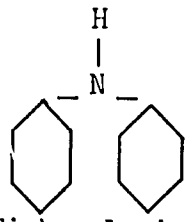


Secondary



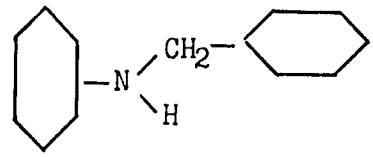
Monomethyl-aniline

or



diphenylamine

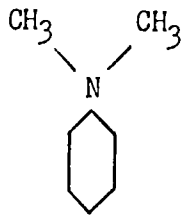
or



benzylphenylamine

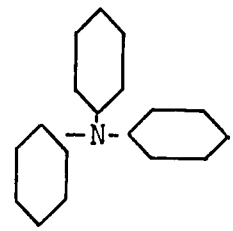
These are examples of various secondary amines.

Tertiary Amines



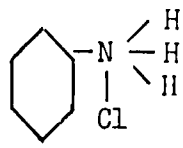
dimethylaniline

or



triphenylamine

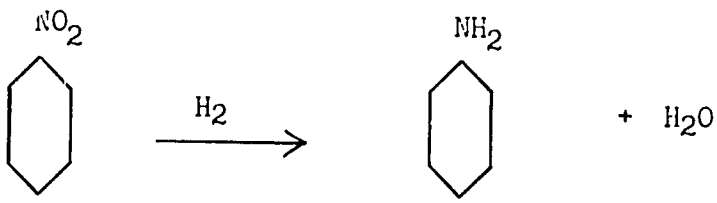
The aromatic amines are also basic due to the presence of the amino group, however they are not as strong bases as the aliphatics. The nitrogen in the aromatic amines in all its normal compounds has a valence of three (3). However, it is possible to form compounds wherein nitrogen shows a valence of five (5). These pentavalent compounds are called salts and are formed by interaction with mineral acids, viz



aniline hydrochloride

Methods of Preparation

The amines are generally prepared by reducing the nitro compounds.



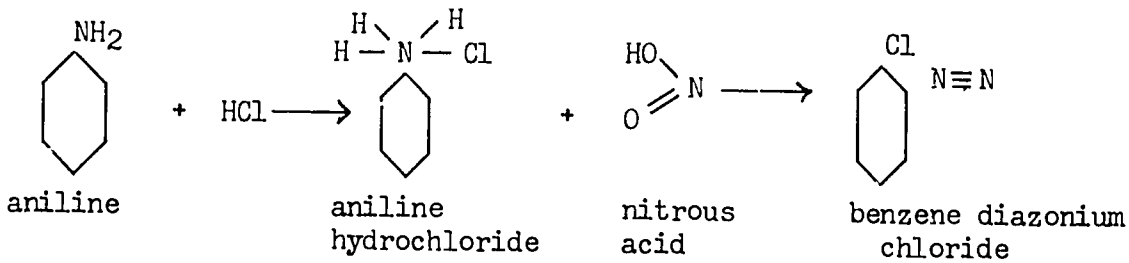
Reaction with Nitrous Acid

The aliphatic primary amines yield alcohol when treated with nitrous acid.

$$CH_3.NH_2 + HONO \qquad CH_3OH + N_2 + H_2O$$

methyl amine + nitrous acid methyl alcohol

But with primary aromatic amines a much different reaction takes place.



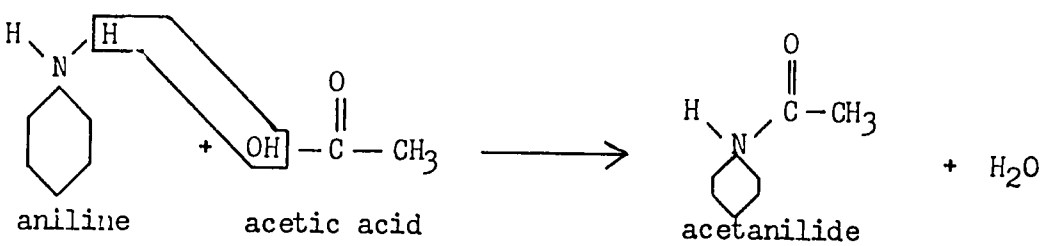
This reaction known as the diazo reaction is a very important reaction.

Various Aromatic Amines

Aniline is the simplest member of this group. It was first manufactured by the distillation of indigo. It also occurs in small quantities in coal tar and bone oil. Industrial production is from nitrobenzene as shown above. The first synthetic dye ever made was made using aniline as the starting material.

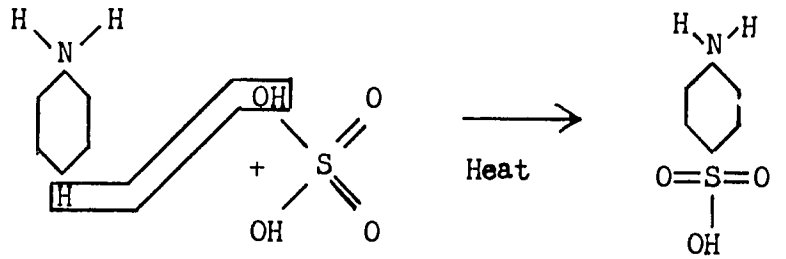
With bromine, aniline forms 2, 4, 6 tribomoaniline

Aniline when treated with glacial acetic acid yields acetyl aniline



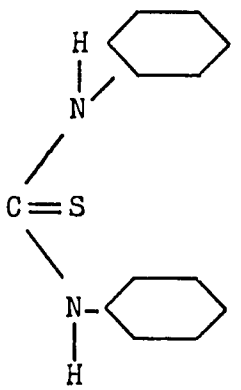
This compound is a medicine used in the treatment of neuralgia and rheumatism. It is also used in headache powders.

With sulfuric acid (H_2SO_4) aniline reacts to form sulfanilic acid. This compound is very important in the manufacture of dyes.



aniline sulfuric acid sulfanilic acid

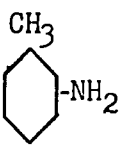
Aniline reacts with carbon disulfide, (CS_2) to form



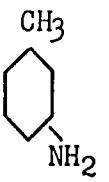
thiocarbanilide

This compound is an "accelerator" used in the vulcanization of rubber.

The toluidines are aminotoluenes, viz



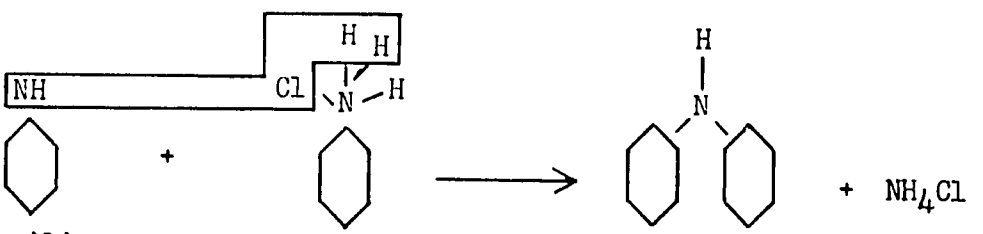
orthctoluidine



metatoluidine

paratoluidine

When aniline and aniline hydrochloride are heated to about 240°C. under pressure, diphenylamine is formed



aniline aniline hydrochloride diphenylamine

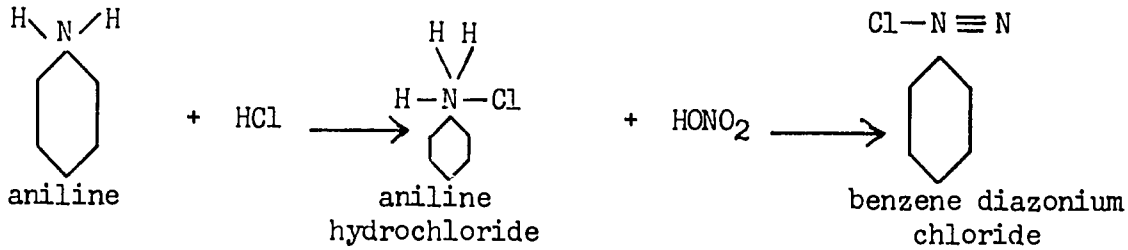
This is also an important intermediate in the manufacture of dyes.

Diazotization

The reaction known as diazotization is one which is peculiar to aromatic amines. It is the reaction which was previously demonstrated under the heading Reaction with Nitrous Acid. Any ring type compound will undergo this reaction provided it has an amino group attached to the ring.

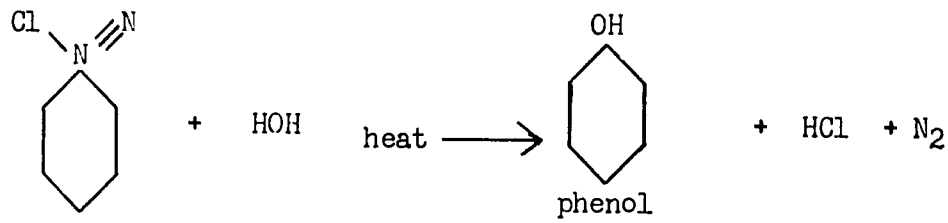
These diazo compounds are very unstable at ordinary temperatures and are usually prepared in an ice bath. They are not generally prepared in the dry state for they are often unstable and explosive.

The following is the diazo reaction again:

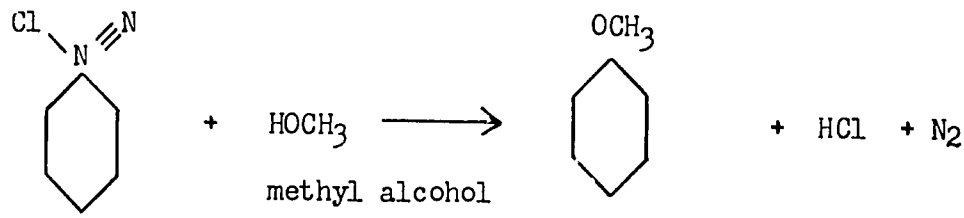


As this diazo compound is a very important intermediate used to form some useful compounds a listing of its reactions is of interest. Many types of aromatic compounds are prepared from these diazonium or diazo compounds.

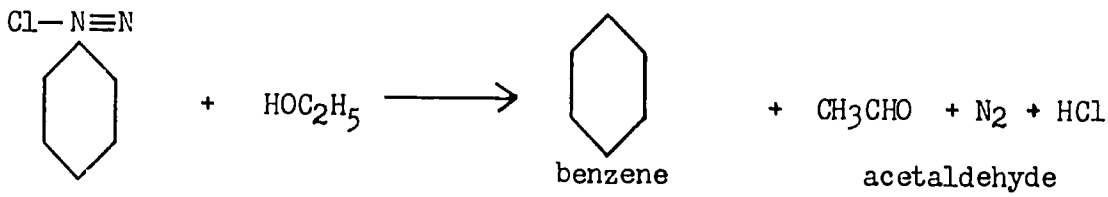
1. Formation of phenol



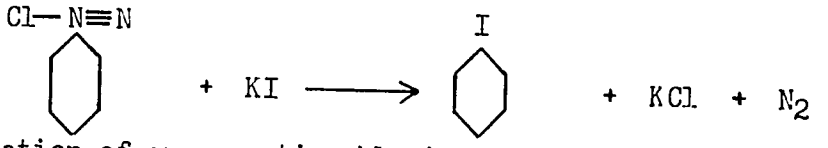
2. Formation of aromatic ethers



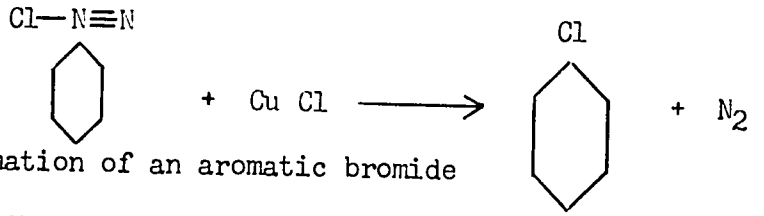
3. Formation of benzene



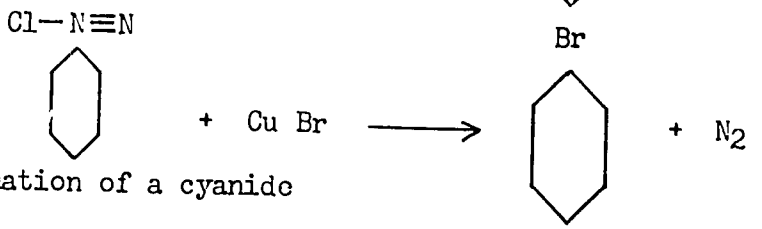
4. Formation of an aromatic iodide



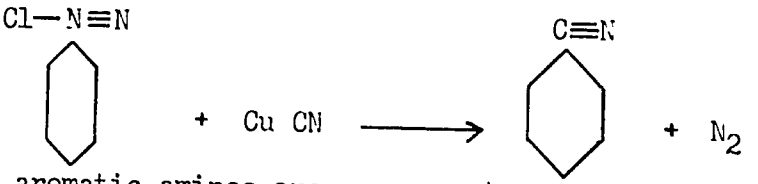
5. Formation of an aromatic chloride



6. Formation of an aromatic bromide

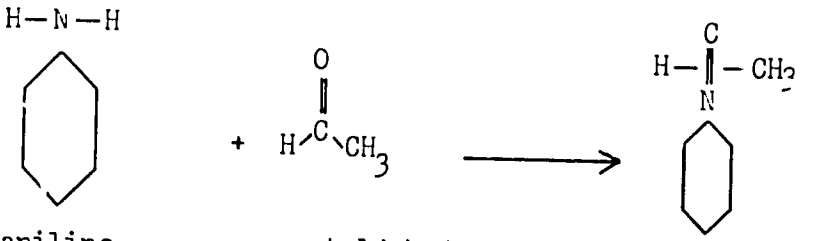


7. Formation of a cyanide



The aromatic amines are very reactive as the previous reactions have demonstrated and just as the aldehydes they condense with other molecules to form compounds which are very important industrially.

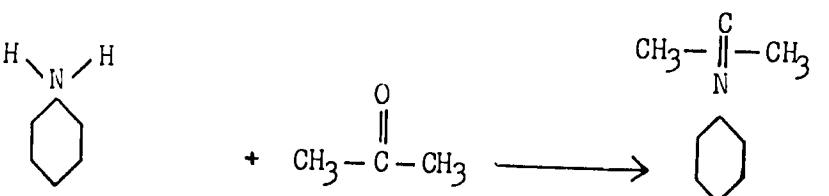
An amine such as aniline readily condenses with aliphatic aldehydes to form compounds which are of use in accelerating the vulcanization of rubber, viz



aniline acetaldehyde acetaldehyde anil

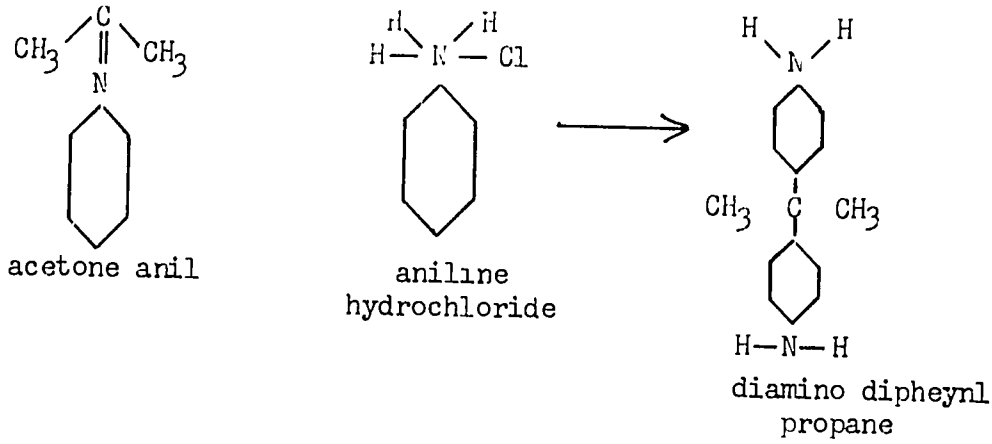
The compounds are called anils.

Aniline will also condense with acetone, just as it did with acetaldehyde for the condensation is with the carbonyl group which is common to both classes of compounds.
viz:



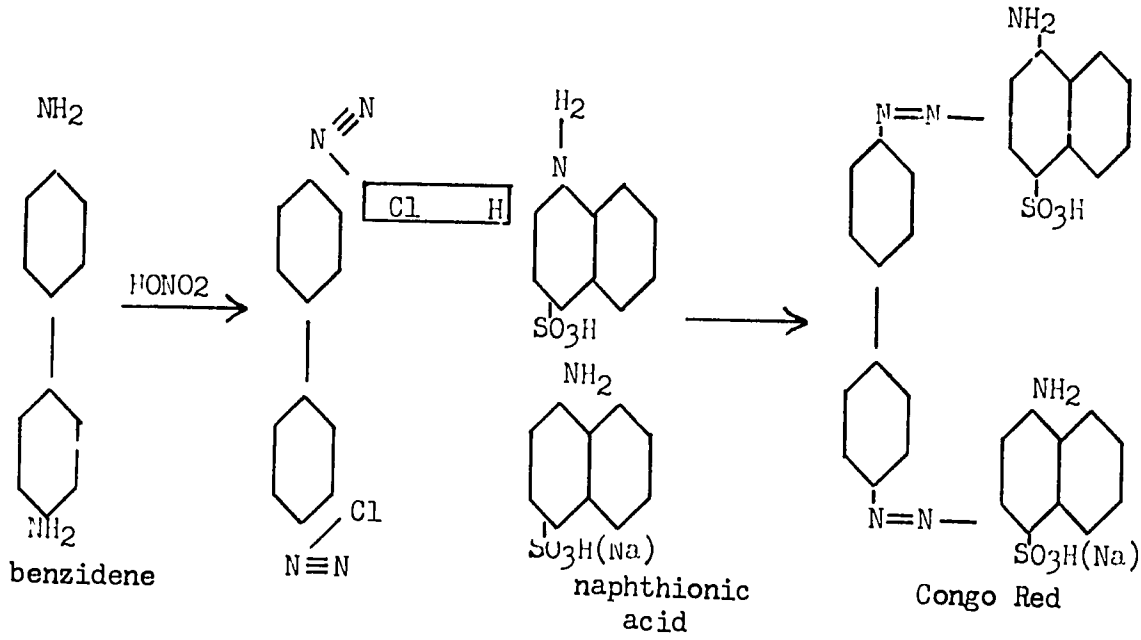
aniline acetone acetone anil

If this acetone anil is condensed with another molecule of aniline hydrochloride further condensation takes place.



This property of the amines to condense makes them good starting materials for plastics. Compounds of this type are now being sold as tanning agents under the name of amino plasts.

The aromatic amines are in many cases the starting point for dyes and dye intermediates. viz:



This is the famous Congo Red dye.

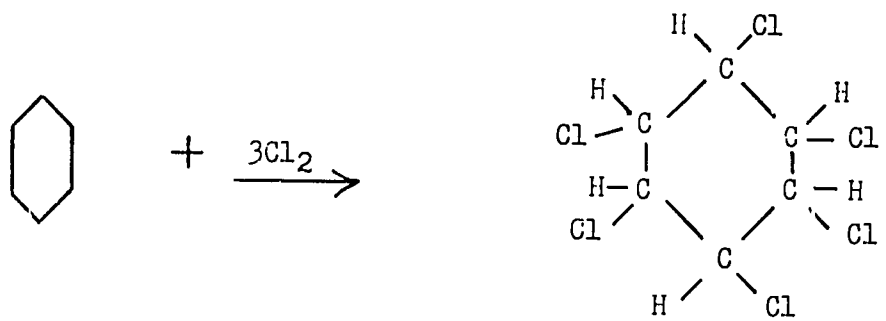
ORGANIC CHEMISTRY

LECTURE 19

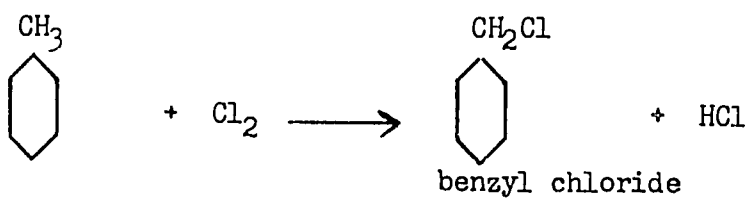
HALOGEN COMPOUNDS

The halogens may react in one of three ways with aromatic hydrocarbons.

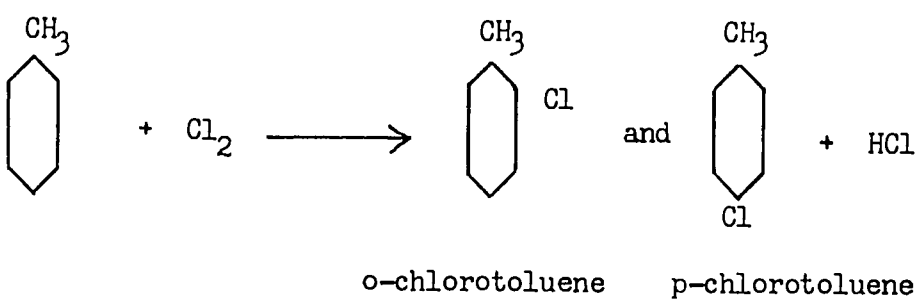
1. Addition (needs sunlight)



2. Substitution in side chain (accomplished at B.P. in sunlight, no catalyst)



3. Substitution in the ring



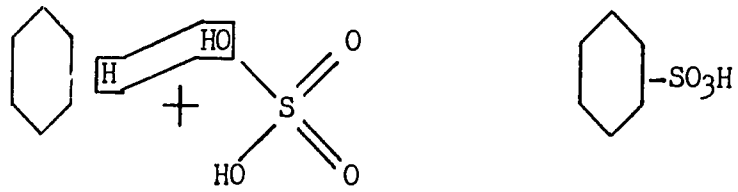
This last needs no heat or sunlight, only a catalyst such as $FeCl_3$, $AlBr_3$, Fe, P, S or I.

Sulfonic Acids

These are an important class of compounds as they are used to prepare phenolic compounds, naphthols, etc.

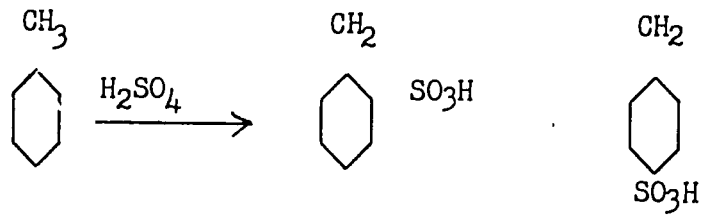
Preparation

1.



benzene sulfuric acid benzenesulfonic acid

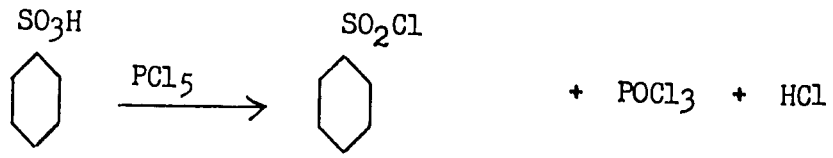
2.



toluene o-toluenesulfonic acid p-toluenesulfonic acid

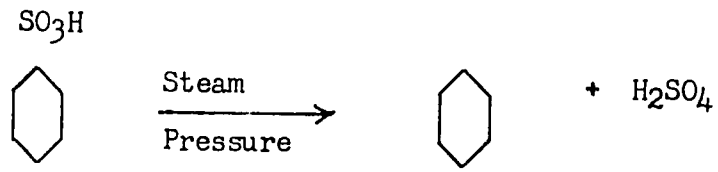
Properties

1.



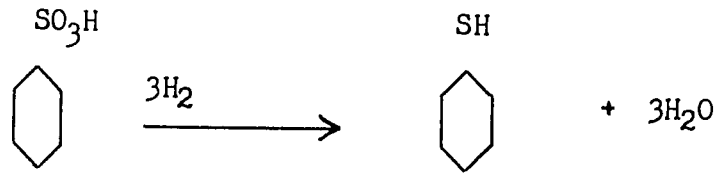
benzenesulfonic benzenesulfonyl chloride

2.



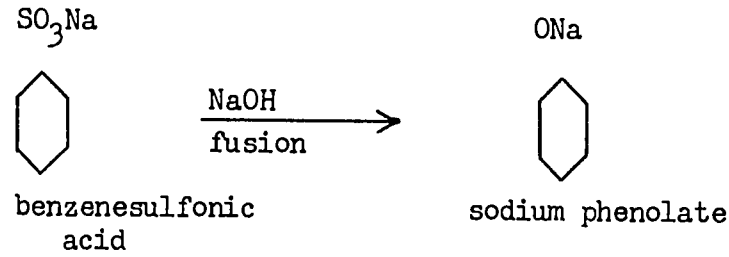
benzenesulfonic acid benzene

3.

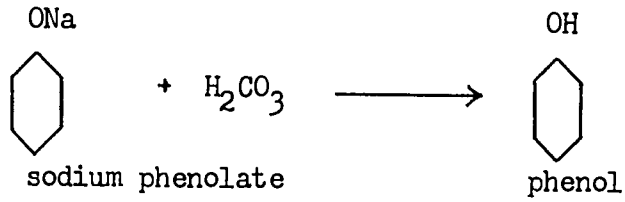


benzenesulfonic acid thiophenol

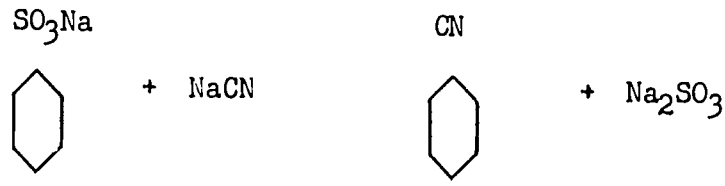
4.



Phenol is obtained by treating with H_2CO_3



5.



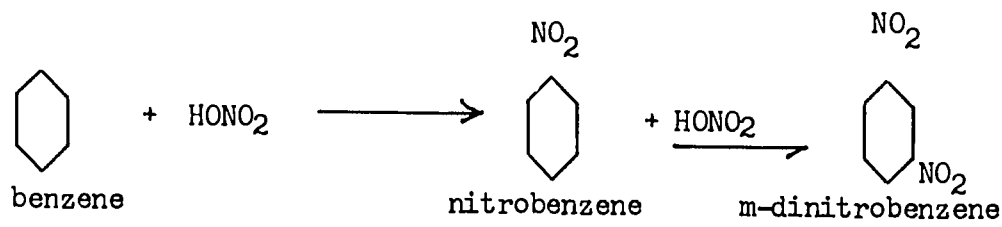
Sulfonation is used in many cases to make organic compounds soluble in water. This is a procedure used in the dye industry.

Nitro Compounds

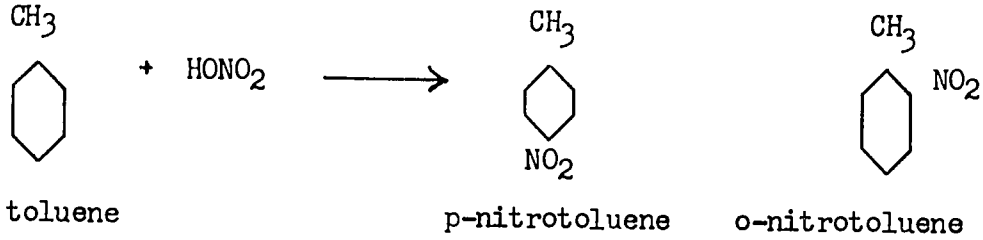
These compounds are prepared by direct treatment with nitric acid. Sulfuric acid is usually present to absorb the water formed.

Preparation

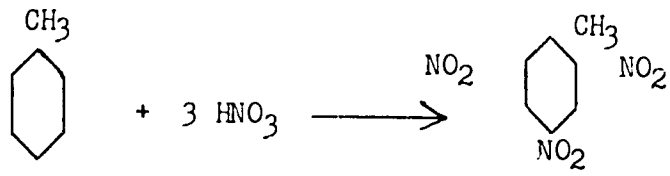
1.



2.



3. If nitration of toluene is carried to completion, complete addition takes place



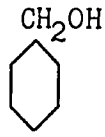
toluene

2-4-6 trinitrotoluene
or T.N.T.

Aromatic Alcohols and Phenols

When the OH, or alcohol group, is attached to a side chain we have an aromatic alcohol; but when it is attached directly to the ring we have a phenol.

viz: 1.



phenyl carbinol
or benzyl alcohol

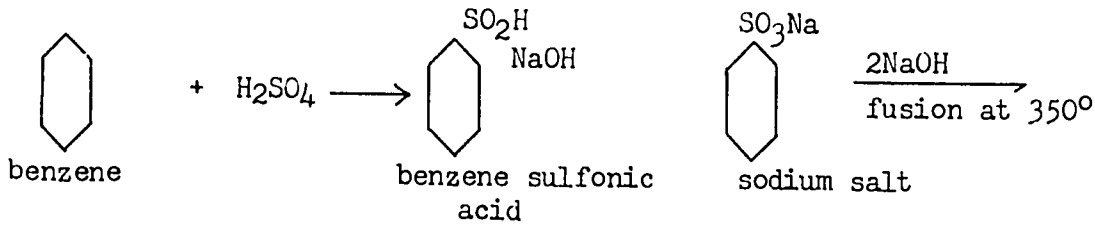
2.

phenyl hydroxide
or phenol

In the aromatic series if the OH group is attached to the side chain the properties of the compound are similar to the straight chain alcohols. These compounds are neutral; that is, they do not ionize.

However, when the OH group is in the ring we get a phenolic compound which acts as a weak acid, that is, a slight amount of hydrogen ion is released in solution.

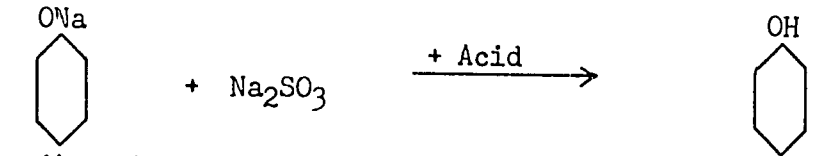
Phenol is found in wood tar and in coal tar. Its most common method of preparation we have already seen under sulfonation.



benzene

benzene sulfonic
acid

sodium salt



sodium phenolate

phenol

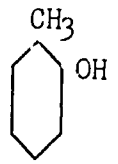
Properties

Phenol is a very weak acid, very corrosive and poisonous. It is commonly called carbolic acid. Some of its reactions are shown on page 240 and 241 of your text.

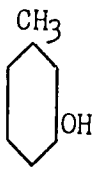
It is a powerful antiseptic, disinfectant and germicide. It is also used in the manufacture of explosives, dyes, developers, medicines and synthetic resins, such as Bakelite.

Cresols

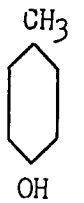
The cresols are substituted phenols.



o-cresol



m-cresol



p-cresol

These compounds are also powerful antiseptics and are used to manufacture explosives, dyes, resins and other organic chemicals. They are found in such preparations as, "Lysol", "Creolin" and "Phenoco".

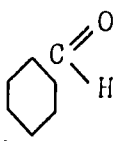
Paradihydroxybenzene or hydroquinone is used in photographic developers.

hydroquinone

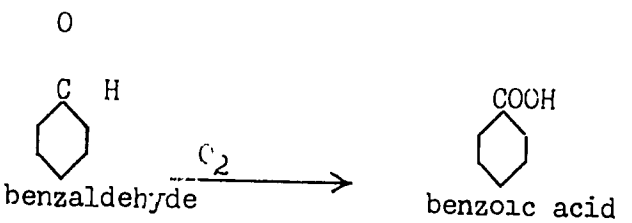
Aromatic Aldehydes

The aromatic aldehydes contain the C(=O)H group just as the aliphatic aldehydes do.

The most important aromatic aldehyde is benzaldehyde.



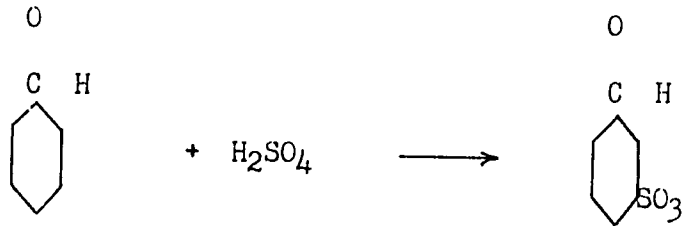
This is called artificial oil of bitter almonds. It readily oxidizes to benzoic acid. (Remember the aliphatic aldehydes oxidize to acids also.)



Properties

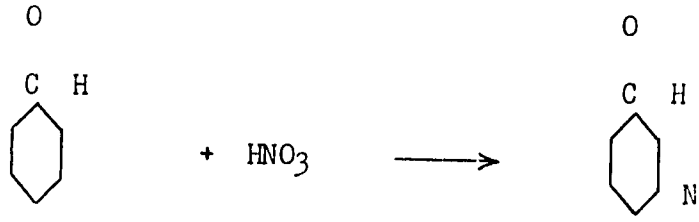
It is possible to sulfonate and nitrate these compounds also:

1.



benzaldehyde m-sulfobenzaldehyde

2.



benzaldehyde m-nitrobenzaldehyde

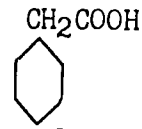
Aromatic Acids

The aromatic acids contain the COOH group attached directly to the ring or to the side chain.

1.

benzoic acid

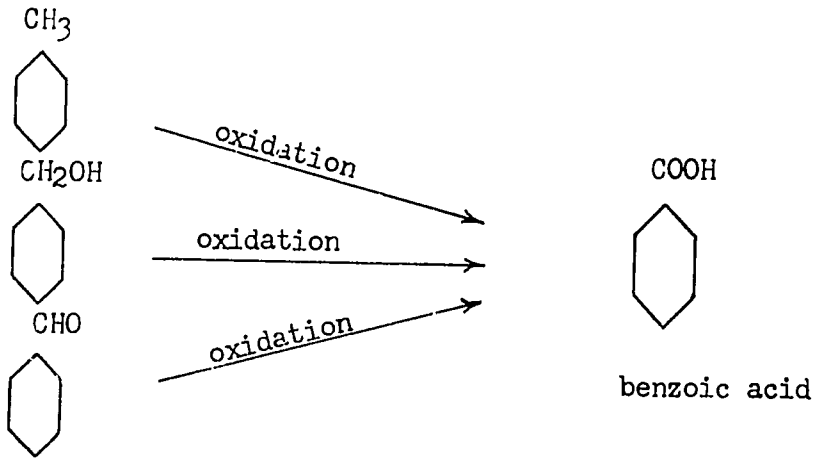
2.



phenyl acetic acid

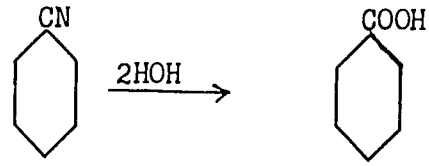
Preparation

Benzoic acid may be prepared by the oxidation of toluene, benzyl-alcohol or benzaldehyde.



benzaldehyde benzoic acid

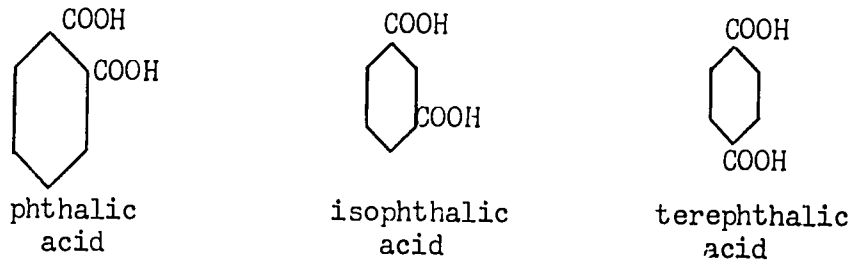
or by hydrolysis of the cyanide:



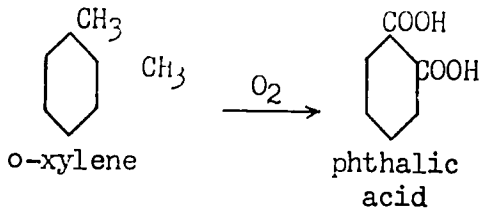
Benzoic acid and similar acids undergo many reactions as shown on Pages 255 and 256 of your text. If you study them closely you will readily see that many of these are the same as the reactions of the COOH group which we studied under the aliphatic acids: that is, salt formation, esterification, chlorination.

But also in addition to these typical acid reactions we can now add the two important reactions of aromatic compounds; that is, sulfonation and nitration.

When two carboxyl groups are found on the benzene ring we have the phthalic acids:

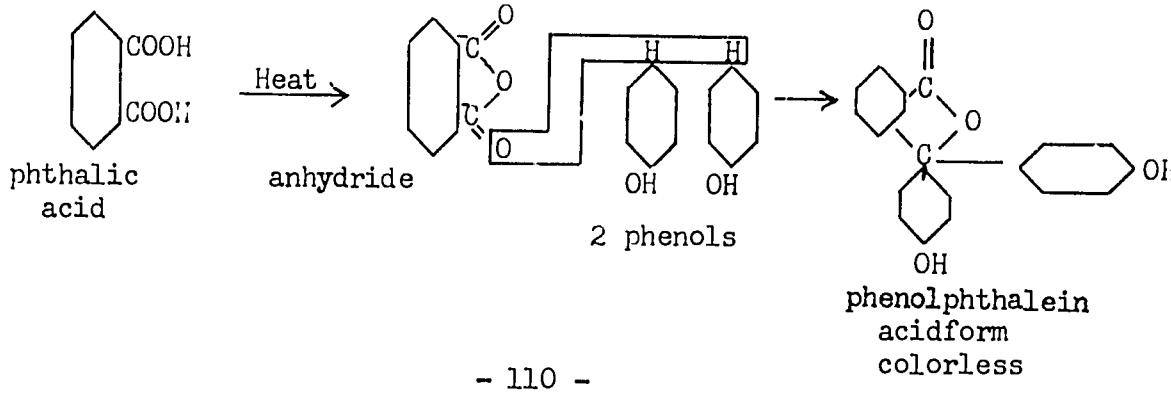


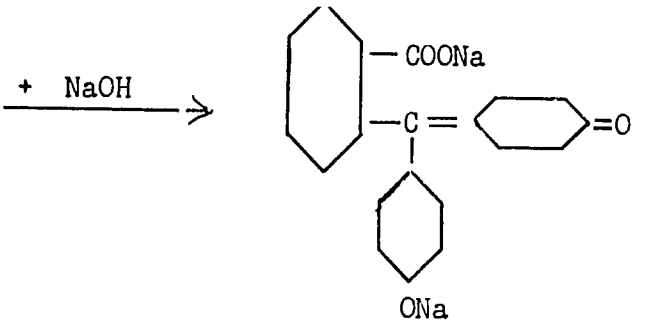
The first, phthalic acid, is used in the preparation of more than 200 compounds. It can be prepared by oxidizing o-xylene.



We have studied many classes of compounds and their particular properties and reactions. We should now be ready to recognize a series of reactions which lead up to the formation of a large or fairly large molecule.

Synthesis of phenolphthalein (an indicator or dye)





quinoid structure
pink

LECTURE 20

DYES AND DYEING

1. What is dyeing?

Placing a material in a water solution of a coloring matter which is of such a nature that it is preferentially absorbed.

Absorbed like a sponge - not dyeing
Painted on surface - not dyeing

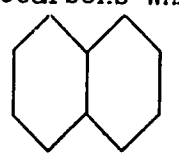
2. What is a dye?

Pigment - an insoluble inorganic colored substance, finely divided.
Color lake - an insoluble inorganic salt of a colored organic acid.
Dye - a soluble colored organic compound which has some kind of affinity for the material to be dyed.

3. Organic structure of dyes.

a. Basic structure - aromatic hydrocarbons which are colorless.

benzene



naphthalene

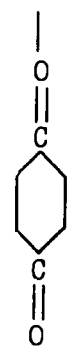
b. Chromophorous groups - certain groups added to the basic structure which make it a colored substance.

$-NO_2$

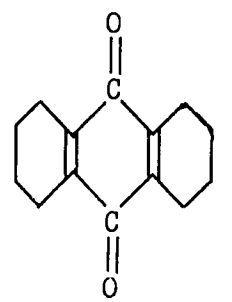
nitro

$-N=N-$

azo



quinone



anthraquinone

c. Auxochrome groups - give salt-forming properties (sometimes also give solubility in water)

$-OH$

phenol

$-COOH$

carboxyl

$-NH_2$

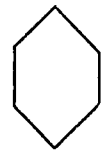
amino

d. Solubilizing groups - make molecule soluble in water

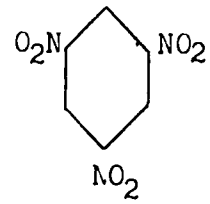
$-HSO_3$ $\qquad$ $-NH_3Cl$

sulfonic acid $\qquad$ amine hydrochloride

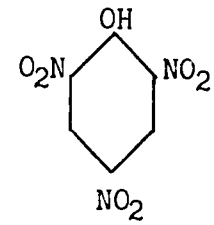
4. Examples of formation of a dye



benzene
colorless
insoluble

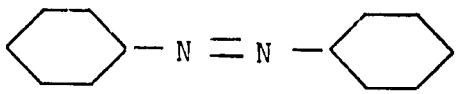


trinitrobenzene
colored
insoluble

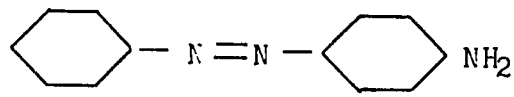


trinitrophenol
(picric acid)
colored
soluble
<u>a dye</u>

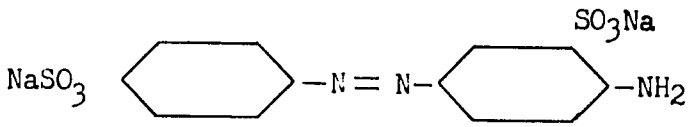
benzene



diazobenzene
colored
insoluble



colored
insoluble
para-aminodiazobenzene



Acid yellow - a dye

5. Two of many types of dyes.

a. Acid dyes - colored molecules solubilized by sulfonic acid groups:

$$D - SO_3Na$$

In water solution, acid dyes ionize:

$$D - SO_3^- + Na^+$$

Note that the colored part of the dye is in the negative ion.

b. Basic dyes - colored molecules solubilize by amine hydrochloride groups:

$$D - NH_2 \cdot HCl \quad \text{or} \quad D \quad NH_3Cl$$

In water solution, basic dyes ionize:

$$D-NH_3^+ \quad + \quad Cl^-$$

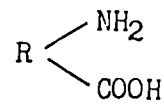
Note that the colored part of the dye is in the positive ion.

6. Leather - a protein

A protein is the condensation product of one or more different alpha - amino acid molecules.

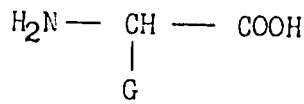
7. Amino acid

A substance which is both an organic acid and an organic base. Contains one or more carboxyl groups and one or more amino groups.



8. Alpha-amino acids

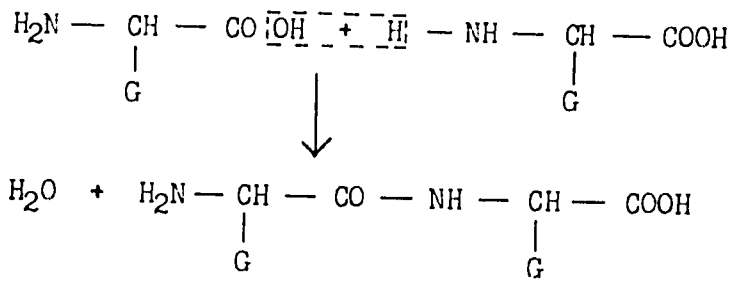
Amino acids in which the amino group is attached to the cargon which is in the α (alpha) position to the carboxyl group:



All alpha amino acids have the same basic structure as above, differ only in the nature of the side-chain "G".

9. Reaction of α - amino acids with each other

a. Since each amino acid has both a basic group and an acid group, a basic group of one molecule can react with the group of another:



The -CO-NH- is called a "polypeptide linkage" and unites two amino acids.

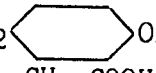
b. This compound still has an amino group at one end and a carboxyl group at the other and can continue to combine with amino acids until very long molecules are formed.

$$-NH-\underset{\underset{G1}{|}}{CH}-CO-NH-\underset{\underset{G2}{|}}{CH}-CO-NH-\underset{\underset{G3}{|}}{CH}-CO-NH-\underset{\underset{G4}{|}}{CH}-CO \quad \text{etc.}$$

These long molecules are called proteins.
Different proteins vary with

a. Length of molecules
b. Nature of the side chains.

10. Nature of the side chains

a. Inert: G = $-CH_3$ (alanine)
b. Alcohol: G = $-CH_2OH$ (serine)
c. Aromatic: G = $-CH_2$  OH (tyrosine)
d. Acid: G = $-CH_2-CH_2-COOH$ (glutamic acid)
e. Basic: G = $-CH_2-CH_2-CH_2-CH_2-NH_2$ (bysine)

11. Amphoteric nature of proteins

a. Since all proteins have acid (-COOH) and basic ($-NH_2$) groups at the ends of the chains and also in the side chains, they are both acid and basic in nature.

b. <u>If</u> there were the same number of acid and basic groups and <u>if</u> the acid and basic groups were equally strong, the protein would be neutral. This is not true. Either the protein has more acid than basic groups or the acid groups are stronger, the protein is acid as compared to water.

c. If a strong acid is added to a protein, in the presence of water:

$$P\begin{cases} COOH \\ NH_2 \end{cases} + HCl \longrightarrow R\begin{cases} COOH \\ NH_3 \end{cases} + Cl$$

Protein now has a positive charge.

d. If a strong base is added to a protein, in the presence of water:

$$P\begin{cases} COOH \\ NH_2 \end{cases} + NaOH \longrightarrow H_2O + P\begin{cases} COO^-Na^+ \\ NH_2 \end{cases}$$

Protein now has a negative charge.

12. There must be one particular pH where the protein is equally positive and negative - this is called its Iso-Electric Point. Iso-electric point of most proteins is between pH 4 and pH 5.

13. Dyeing of proteins

a. On acid side of iso-electric point, protein has a positive (+) charge.

b. On alkaline side of iso-electric point, protein has a negative (-) charge.

c. Acid dyes have color in negative ion.

d. Basic dyes have color in positive ion.

e. If dye bath is on acid side of iso-electric point, protein and basic dye will have same charge - no dyeing will result; protein and acid dye have opposite charges - dyeing will occur.

f. If dye bath is on alkaline side of iso-electric point (not necessarily alkaline to water) protein and acid dye will have same charge - no dyeing will occur; protein and basic dye have opposite charges - dyeing will occur.

g. Electrical attraction deposits dye on surface of protein as above - this occurs very rapidly; but if this were all that occurred, the dye would be left on the surface and would rinse or rub off easily.

h. As dyeing continues, and if the protein is swollen, dye migrates into the interior of the protein and deposits on $-NH_2$ or -COOH groups (penetration). On rinsing or rubbing, dye will not now rub off.