CIVE 3331 - ENVIRONMENTAL ENGINEERING
Spring 2003

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Purpose: Lecture #5 CIVE3331

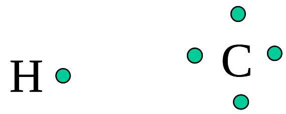
Organic Chemistry

Organic chemistry refers to chemistry involving carbon atoms. It is a varied and complex field – most of the things in our daily lives are related to or dependent on organic chemistry: food, fuels, textiles, adhesives, pesticides, filters, etc. In this lecture only a cursory examination of organic chemistry is made – the principal goal is to familiarize you with naming conventions and structural drawings so that these names and drawings are not so foreign when they appear later in the course or other courses.

Bonding

In chemicals two kinds of bonds are common – ionic and covalent. Covalent bonds are the sharing of electrons in the outer shells of each atom to gain the thermodynamically preferred "noble element" state in the outer shell. Many organic chemicals have both kinds of bonds, but the covalent bonds are by far the more examined bonds in organic chemistry. Examples of organic ionic bonds are certain kinds of acids and bases that donate protons from a organic backbone, but the protons disassociate in the same fashion as strong inorganic acids. (Sulfuric acid has many organic analogs, where there is a sulfonated organic backbone and two protons that disassociate easily).

A Lewis structural diagram is one way of representing atomic bonds that are present in molecules of compounds of interest. Lewis diagrams have the symbol of the atom surrounded by small dots that represent the outermost orbital (valence) electrons.



In covalent bonding theory the atoms share electrons to achieve the configuration of a noble element (8 electrons in the outer orbital). Thus butane (4 carbon gas) would have the following Lewis structure.

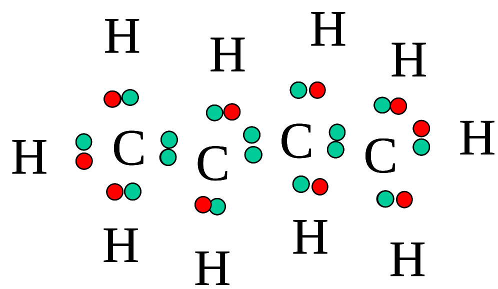


Figure 1. Lewis Structure for Butane

The green dots are the electrons associated with the carbon atoms and the red dots are the electrons associated with the hydrogen. In this picture the sharing is obvious – in practice we don't care about the "color" of the dots and don't distinguish the source of the electrons.

A simpler way to represent the same structure is to use a small line segment to represent electron pairs. This approach is the most "conventional" representation of organic structures when such structures are studied.

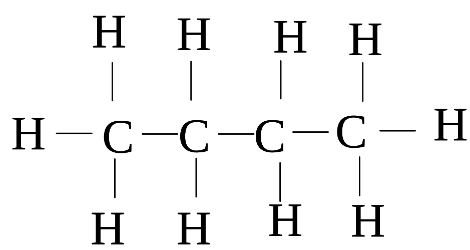


Figure 2. Conventionial Structure Diagram for Butane

Still another way is to represent each carbon as the vertex of a line segment, where the line segments represent electron pairs.

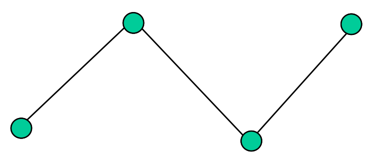


Figure 3. Kinky diagram for butane (C emphasized by dots)

In practice, we don't bother with the dots shown in Figure 3, they are included just to illustrate that the ends of a segment is a vertex (Carbon).

In these three examples the compound is n-butane (all carbons in a single chain). An alternate structure with the same chemical formula is called an isomer. In all cases, isomers will have different physical and chemical behavior form one another.

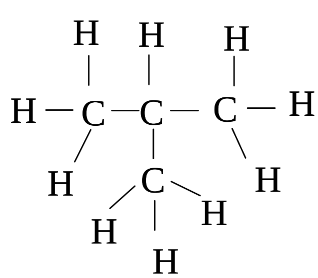


Figure 4. Iso-butane diagram (1 of 2)

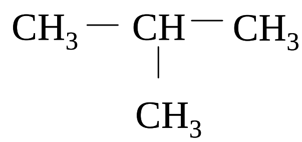


Figure 5. Iso-butane (alternate structure diagram 2 of 2)

For butane, the isomer is iso-butane, and one carbon branches from another carbon as in Figure 4. An alternate diagram is shown in figure 5, both figures 4 and 5 are typical representations of physical structures in organic chemistry.

Butane is an example of a compound that contains only carbon and hydrogen. These compounds are called hydrocarbons. If the hydrocarbon's carbon atoms form single bonds with other atoms it is called a saturated hydrocarbon, paraffin, or alkane.

-ane refers to a series of hydrocarbions starting with methane (CH_4), then ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}), and so on.

1. C_1 – C_4 are gasses
2. C_5 - C_{20} are liquids (includes components of gasoline and diesel)
3. C_{21} - are waxy solids (paraffin)

Hydrocarbons are building blocks of many chemicals. For example start with ethane

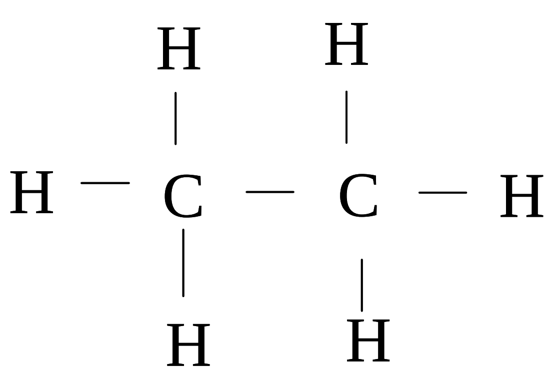


Figure 6. Ethane

Substitute one Cl for a H

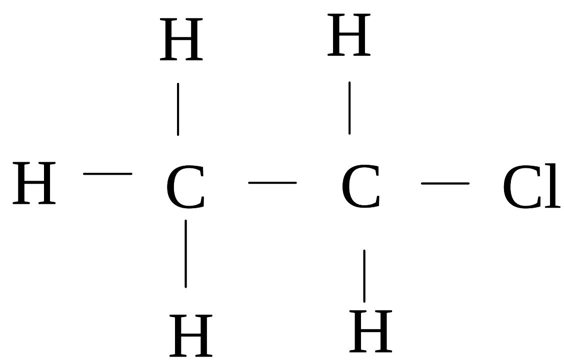


Figure 7. Chloro*ethane*

Substitute a second Cl for another H

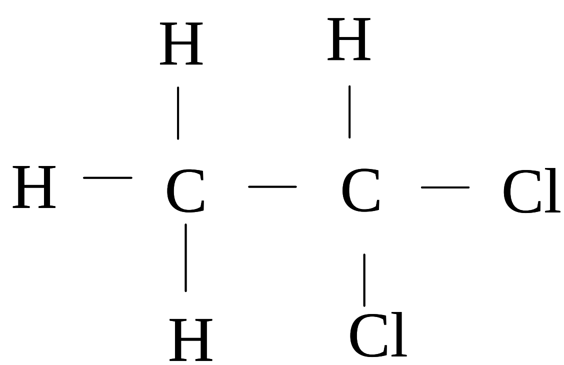


Figure 8. 1,1-Dichloro*ethane*

Substitute a third Cl for another H

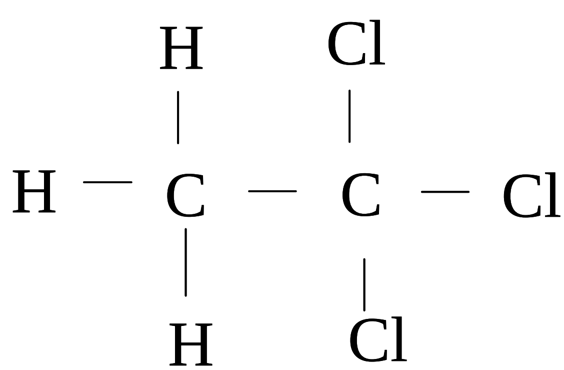


Figure 9. 1,1,1-Trichloroethane (TCA)

This last compound is a popular industrial solvent used for degreasing metal parts and certain plastics. It is also a common groundwater contaminant. These compounds are all saturated hydrocarbons.

An unsaturated hydrocarbon has at least 2 carbon atoms joined by a multiple bond.

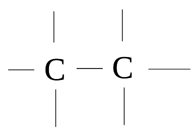


Figure 10. Ethane (saturated carbons)

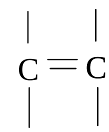


Figure 11. Ethylene (unsaturated carbons - share a double bond)

The double bond series starting with ethane is called the alkene series.

Functional groups

The substitutions of different chemicals in place of hydrogen are sometimes recognized as “functional groups.” The name comes from the observation that these “groups” change chemical or physical function or engage in reactions as an entire group and not as component atoms.

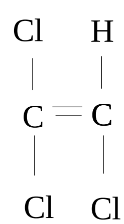


Figure 12. tri-chloroethylene

In the case of ethane, if three chlorines are substituted onto the compound we get tri-chloroethylene (TCE), another very common industrial solvent and groundwater contaminant.

In addition to single atom substitutions, functional group substitutions are also important.

-OH group produces an alcohol; -O- between carbons produces an ether; H-C=O produces an aldehyde; -OH onto a C=O produces a carboxylic acid; $-NH_2$ group produces an amine.

Some structural diagrams are:

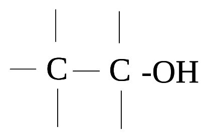


Figure 13. Ethanol (ethyl alcolhol)

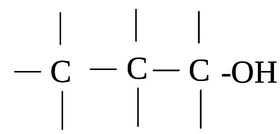


Figure 14. Propyl alcolhol (rubbing alcolhol)

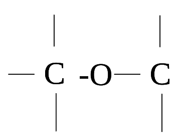


Figure 15. Dimethyl ether

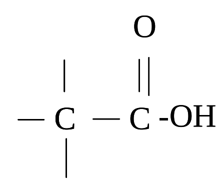


Figure 16. Acetic acid

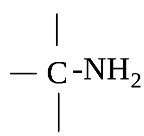


Figure 17. Methyl amine

Hydrocarbons can have linear, branched or loop (ring) structures.

Benzene is an example of a ring structure. Molecules with ring structures are also called aromatic compounds.

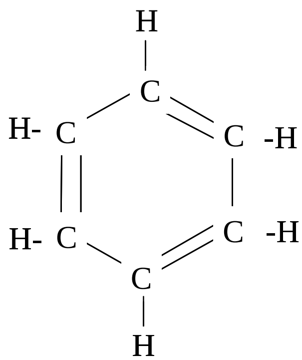


Figure 18. Benzene structural diagram

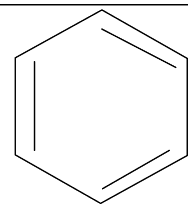


Figure 19. Benzene structural diagram (alternate)

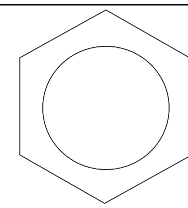


Figure 20. Benzene structure (alternate)

When the benzene ring is part of a larger molecule, it becomes a functional group called a phenyl group.

Attachment locations determine naming in ring structures;

1. Ortho- adjacent
2. meta – one space between
3. para – across (equal spaces between of even # carbons)

Naming compounds is complex and important. The names identify functional groups as well as structure – this knowledge can be exploited in environmental treatment processes.

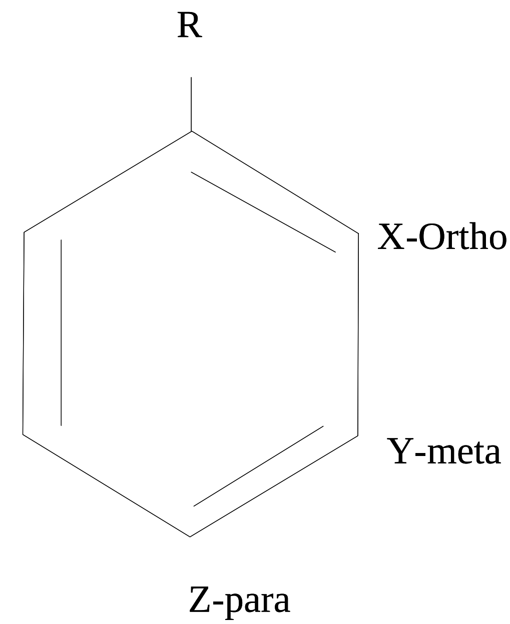


Figure 21. Attachment locations and naming - relative to R

<u>Nuclear Chemistry</u>

A lot of chemicals of environmental interest are those that undergo radioactive decay – the chemistry and physics of decay is called nuclear chemistry.

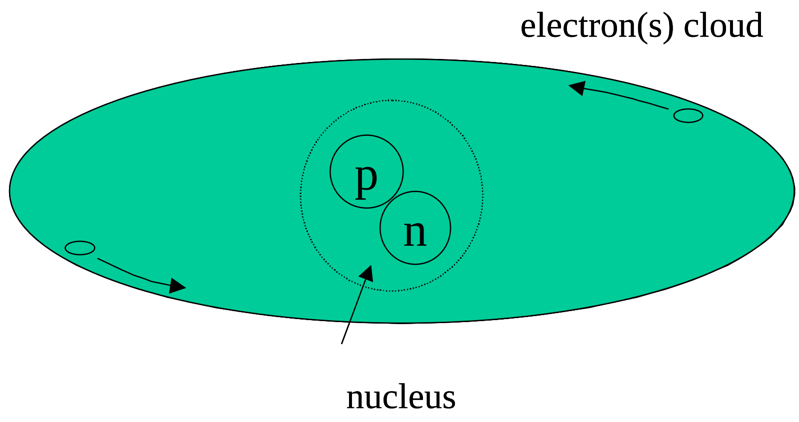


Figure 22. Cartoon of Atom

Mass number is the sum of protons and neutrons in the atom.

Atomic number is the number of protons

Notation convention is the mass number superscript, atomic number subscript as in following examples.

${}^{235}_{92}U; {}^{238}_{92}U$ - isotopes of uranium. ${}^{238}_{92}U$ has three more neutrons than U-235.

A technique called gaseous diffusion is used to enrich uranium with respect to the 238 isotopes. The diffusion process works because the higher mass compound diffuses slightly slower than the lower mass compound. By manipulation of the diffusion process it is possible to create a sample enriched with respect to U-238. A gaseous diffusion plant is huge, so it is a very expensive undertaking.

Many isotopes are unstable, and discard excess particles and energy in an attempt to reach a stable compound. Such "decay" is called radioactive decay. There are three recognized froms of atomic radiation:

1. alpha – 2 proton, 2 neutron (helium nucleus) ${}^{4}_{2}a$
2. beta – electron (created by n => proton + electron)
3. gamma – photons (very high energy EM particle)

The range of penetration (and tissue damage to living critters) is inversely proportional to mass. Alpha is heavy, low penetration. Gamma has zero mass, very high penetration. In addition to penetration, of the energy can ionize tissue the damage is more dangerous –all three kinds of atomic radiation are ionizing.

A decay chain is a list of decay particles and compounds an unstable atom passes through during its decay.

For example plutonium decays into uranium an alpha and a gamma.

$${}^{239}_{94}Pu \rightarrow {}^{235}_{92}U + {}^{4}_{2}a + g$$

Strontium decays into ybrittium and a beta. (Strontium is especially problematic because it nicely substitutes for calcium in bone tissue and can cripple the immune system because of bone marrow destruction)

$$^{90}_{38}Sr \rightarrow ^{90}_{39}Y + b$$

Not all compounds of a compound decay simultaneously or instantly. The spontaneous decay happens randomly (with respect to when and which atom decays). The time required for half of the original atoms to decay in a sample is called the half-life of the sample (or substance). A given isotope has a unique half-life, but the half-lives of known isotopes ranges from fractions of a second to hundreds of thousands of years.

Units of radioactivity

Ci (Curie) = 3.7 x 10 10 decay events/second (rate)

Bq (Becquerel) = 1 decay event/second (rate)

R(Roentgen) = ionizations produced by X or g rays (dose/effect)

Rad (radiation absorbed dose) = 100 ergs/gram (energy/mass absorbed – dose)

Rem (roentgen equivalent man) = effect of a particular rate * time (dose) on humans.

Fission

Fission is energy released when atoms are spilt in a nuclear reaction.

Heavy atoms => lighter atoms + energy (a lot of energy)

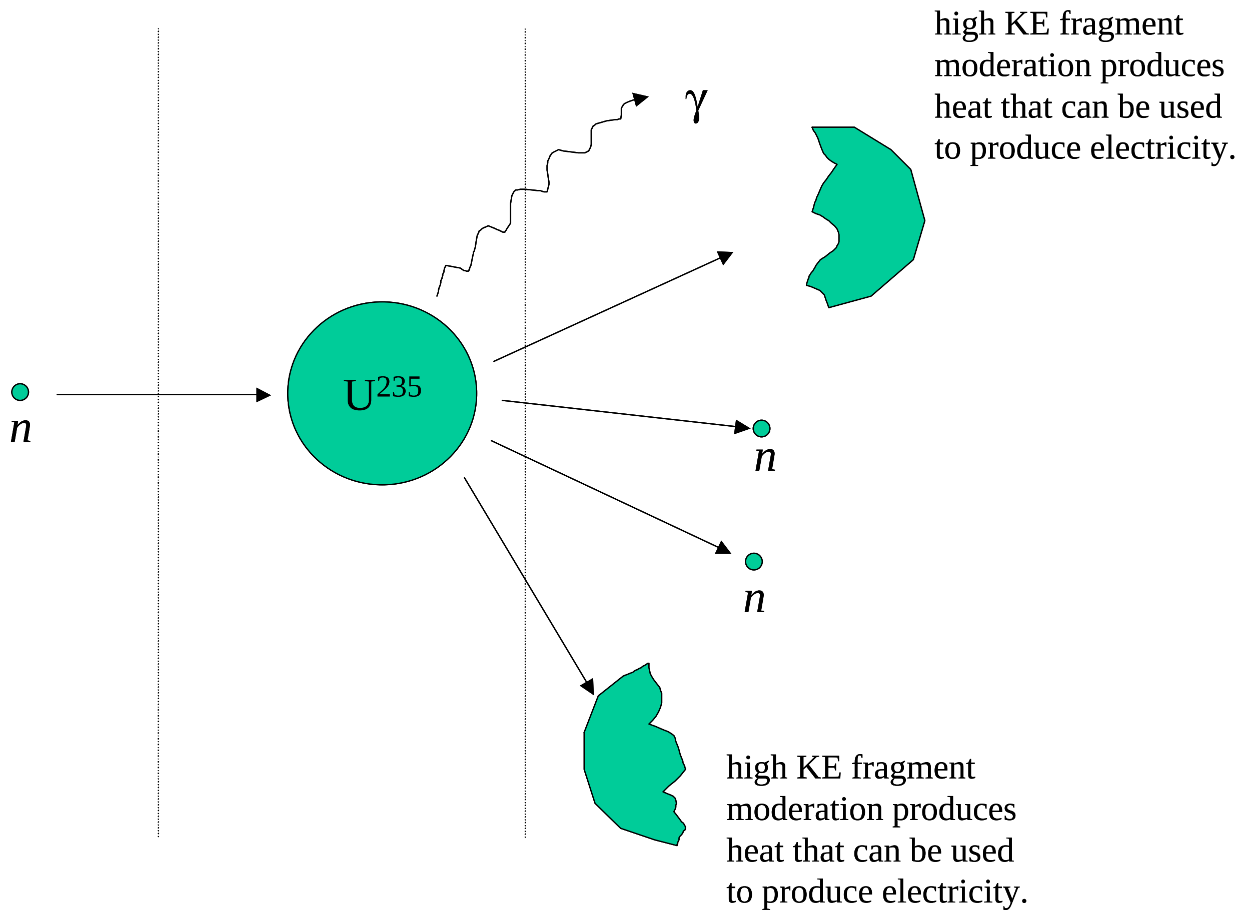


Figure 23. Fission reaction

Fusion

Fusion is energy released when atoms are joined in a nuclear reaction.

Light atoms + light atoms => heavy atoms + energy (a whole lot of energy!)

To date there have been no successful, sustained, controlled fusion reactions that produce net energy for very long. Best experiments produce net energy for seconds at best and are a challenging area of energy research. When controlled fusion is cracked, many energy issues globally will be greatly changed. Hydrogen bombs don't count, its not a very controlled release of energy!

Fuel Cells

No discussion of energy is complete without introduction of a fuel cell. Is is a non-nuclear “fusion” of lighter components in an electron transfer reaction. We don’t get nuclear magnitudes of energy but it is a useful concept none the less.

Consider the reaction of hydrogen and oxygen (just like in a rocket)

$$2H_{2(g)} \quad + \quad O_{2(g)} \quad = \quad 2H_2O_{(l)} + \quad heat$$

Now if we perform this reaction in a rocket nozzle, the heat released is directed downward and the “liquid” ejects at an enormous speed. The conservation of linear momentum makes the rocket move forward (but that’s just physics!).

If we perform this reaction in an electrolytic cell (perhaps across a thin membrane) the energy released is not heat, but useful work as the electron transfer in the reaction is passed through a resistive load (lamp, motor, etc.)

If we calculate the change in enthalpy of the reaction we can get an idea of the energy involved.

$$2H_{2(g)} \quad + \quad O_{2(g)} \quad = \quad 2H_2O_{(l)} + \quad heat$$

$$0 \qquad 0 \qquad \Rightarrow \qquad 2(-285.8 \text{ kJ/mol})$$

The change in enthalpy is negative thus this reaction liberates energy.

Fuel cells will probably become commercially viable in the next decade for terrestrial –consumer use. The principal engineering challenges are the storage of the hydrogen (metal hydride absorbents are likely) and the conversion of hydrocarbon and waste gasses into hydrogen rich fuels. The hydrogen-oxygen is not the only possible fuel cell, there are others that can directly use hydrocarbons, but their operating temperatures are too high for consumer use.

Document History:

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