Alkanes

An alkane is a hydrocarbon (composed of only carbon and hydrogen) that possesses the simplest empirical formula for organic compounds that do not contain a functional group.

All alkanes have the general formula: $C_n H_{2n+2}$.
Alkanes are named according to IUPAC. The rules define a prefix that shows the number of carbon atoms and a suffix that defines the functional group. In the case of alkanes, there is no functional group and the suffix is *–ane.* The prefixes are based on the Latin numbers for 1-20 that correspond to the number of carbon atoms. Methane (n = 1) is the first member, ethane (n = 2) the second member, propane, butane followed by pentane, and so forth… (Greek prefixes are used for the alkanes from pentane onwards.)

Alkyl groups are formed by the removal of a hydrogen from an alkane. They are named by replacing the ending –ane in the corresponding alkane by *–yl*, as in methyl, ethyl, and propyl. Some older nomenclature use the prefixes *sec*- (or s-), which stands for secondary, and *tert*- (or t-) , for tertiary. To understand the prefixes of primary, secondary and tertiary in organic chemistry ...

A *primary* carbon is one attached to only one other carbon atom, hydrogens attached to such a carbon atom are designated as primary hydrogens,
A *secondary* carbon is attached to two other carbon atoms, and
A *tertiary* carbon to three other atoms. Their hydrogens are labeled similarly; finally,
A *quaternary* carbon is attached to four alkyl groups.

Iso: $-CH(CH_3)_2$
sec: $-CH+CH_3+$an alkyl group (not a methyl)
tert: $-C+(CH_3-)_2+$alkyl (maybe methyl)

The total number of carbon atoms dictates the name (isopropyl for three C- atoms, isobutyl for four C- atoms). When the *$-C(CH_3)_3$ group is at the end of the chain*, it is called *neo-*, as in neopentyl for the five carbon fragment.

The alkanes form a homologous series: they can be represented by a general formula, each member differs from the next lower one by the addition of a methylene group, $-CH_2-$.

What do the structures of alkanes look like in three dimensions?

The carbon atoms are sp^3 hybridised, tetrahedral, with bond angles close to 109° and with regular C-H (~1.10 A°) and C-C (1.54 A°) bond lengths. Alkane chains often adopt the zig-zag patterns used in bond –line notation, example: propane: 

What are the general properties of alkanes?

Alkanes lack functional groups, as a result, they are relatively non-polar , since the electronegativities of carbon and hydrogen are 2.5 and 2.1 respectively and.
Alkanes are thus non-polar molecules, only van-der-Waals forces come into play. The attractive forces are so weak that the lower alkanes from CH_4 to C_4H_{10} are gases at room temperature and pressure. The alkanes C_5H_{12} to C_{17} are liquids, while those with larger molecules are solids.

Alkanes are generally insoluble in water or other highly polarized liquids, liquids alkanes are less dense than water. The higher members are viscous liquids, and viscosity increases with increasing molecular mass as the attractive forces between molecules increase.
They have no functional group and therefore, associate in the liquid phase only by van-der-Waal's forces, leading to low boiling points. Once the mass of the alkane is sufficiently large, however, the boiling point also becomes rather high, very large alkanes are solids.
That is, to say, melting points, boiling points, and densities increase with molecular mass because of increasing attraction between molecules.

Note: Branched alkanes have smaller surface area than their straight-chain counterparts (isomers), as a result they experience smaller London attractions and are unable to pack as well in the crystalline state. The weaker attractions result in lower melting and boiling points for branched chain isomers.

Structural Isomers

Isomers refers to two or molecules that have the same empirical formula but the individual atoms are connected in different ways, leading to different molecules, example for butane, C_4H_{10} there are two isomers possible ...

Why is the concept of isomerism important for alkanes?

Due to the ability to form isomers, there are literally millions of possible alkanes. As the number of carbons increase, the number of constitutional isomers increases dramatically: 2-methylpropane, C_4H_{10} is isomeric with butane, three for pentane, five for hexane, nine heptanes, and 18 for octane, 35 for nonane, 75 for decane, etc.

Since isomers will be different molecules with different physical properties (mp, bp, solubility, etc.), $\therefore$ it is necessary to distinguish one molecule from all other isomers.

Isomers of different alkanes:

Carbon atoms	Isomers
4	2
5	3
6	5
7	9
10	75
20	366 319

Reactions of Alkanes

Alkanes are generally inert, they do not react with acids, bases, oxidising and reducing agents, nucleophiles, electrophiles or polar reagents.

1. Combustion

Alkanes burn in an excess supply of oxygen to form the harmless products carbon dioxide and water$_{(l)}$, in a highly exothermic reaction:

$$CH_{4(g)} + 2\,O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)} \qquad \Delta H^{\theta} = -890 \text{ kJ mol}^{-1}$$

Liquid alkanes such as octane must be vaporized before they will burn:

$$C_8H_{18(g)} + 12\tfrac{1}{2}O_{2(g)} \longrightarrow 8\,CO_{2(g)} + 9H_2O_{(l)} \qquad \Delta H^{\theta} = -5510 \text{ kJ mol}^{-1}$$

This reaction takes place in the internal combustion engine. The enthalpies of combustion are important, because most of the shorter chain alkanes are used as fuels, example CH_4: natural gas, C_3H_8: camping gas.

In a limited supply of oxygen, the poisonous gas carbon monoxide is formed. With even less oxygen available, carbon is deposited as soot, (as observed by you many a time when you heat a test tube using a Bunsen with its air-hole closed. Soot is also formed in the exhaust pipes of cars whose engines have been running on an over-rich mixture., for example with the choke left out.

The energy of light quanta

The energy of a quantum of electromagnetic radiation is given by: $E = hf$ where h is the Planck's constant, 6.626×10^{-34} Js, and f is the frequency of the radiation.

For a typical quantum of ultraviolet light, $f = 1 \times 10^{15}\ s^{-1}$, so

$$E = (6.6 \times 10^{-34}\ Js)(1 \times 10^{15}\ s^{-1}) = 6.6 \times 10^{-19}\ J$$

Since, 6×10^{23}, the Avogadro's constant, is the number of particles in a mole, hence for 1mole of quanta the total energy is:

$$= (6.6 \times 10^{-19}\ J)(6 \times 10^{23}\ mol^{-1})$$
$$= 396\,000\ J\ mol^{-1}$$
$$= 396\ kJ\ mol^{-1}$$
$$\text{i.e.} \sim 400\ kJ\ mol^{-1}$$

Visible light has a typical frequency of 1x10^{14} s^{-1} and infra-red (heat) radiation 1x10^{13} s^{-1}.

So, the energy of their quanta are respectively 40 and 4 kJ mol^{-1}.

Typical covalent bond energies (See Data Book: Table 10) are ~ 300 kJ mol^{-1}, so visible and infra-red radiations are unable to break covalent bonds while ultraviolet light can break covalent bonds!!!

Calculate the wavelength of light (in nm) required to break a Cl — Cl and a C — C bond (Planck's constant, h, = 6.626 x 10^{-34} Js, speed of light, c = 2.998 x 10^{8} kJ mol^{-1})

λ = ch /E   For a Cl — Cl bond, λ = 494 nm   (Data Book, E = 242 kJmol^{-1})
For a C — C bond, λ = 344 nm   (Data Book, E = 348 kJmol-^{1})

Thus, the energy to break the Cl – Cl bond is in the violet part of the visible spectrum. Hence, Cl_2 molecules are not likely to exist for long in the atmosphere, where they can be broken apart by visible light.

2. Reaction with halogens

Alkanes do not react with halogens in the dark at room temperature, but react in the presence of sunlight. For example, a test tube containing hexane and a drop of liquid bromine, retains the red-orange colour of bromine in the dark. However, if the solution is exposed to sunlight, the colour fades and acidic fumes of hydrogen bromide gas can be detected; suggesting that a substitution reaction has taken place: since the hydrogen in the $HBr_{(g)}$ must have come from the alkane. The overall reaction is:

$$C_6H_{14(l)} + Br_{2(l)} \longrightarrow C_6H_{13}Br_{(l)} + HBr_{(g)}$$

Since this reaction takes place in the presence of light, it is called a **photochemical** reaction. Alkanes can be chlorinated and brominated photochemically.

The mechanism for this reaction is based on the following evidence:

1. Reaction takes place rapidly in the presence of sunlight, but not in the dark at room temperature.
2. A little ethane, C_2H_6, is also formed.
3. If a trace of tetramethyllead, $Pb(CH_3)_4$, is added, the reaction will take place in the dark or at room temperature. This substance is known to dissociate into methyl radicals, $CH_3\bullet$

A mechanism for the chlorination of methane, which fits these observations is as follows:

1. Energy absorbed from light allows the homolytic fission of the Cl– Cl bond, (242 kJ mol^{-1}), rather than the C– C bond (435 kJ mol^{-1}) ...

$$Cl — Cl \xrightarrow{\text{light or heat}} 2\ Cl\bullet \qquad \text{(photochemical homolysis)}$$

2. The chlorine radical formed may then undergo two possible reactions ...

$$\text{Cl}\bullet + \text{CH}_4 \longrightarrow \text{CH}_3\text{Cl} + \text{H}\bullet$$
$$\text{Cl}\bullet + \text{CH}_4 \longrightarrow \text{HCl} + \bullet\text{CH}_3$$

The second possibility is far more likely because the formation of the H – Cl bond is highly exothermic, (431 kJ mol^{-1}), than the formation of a C – Cl bond, (350 kJ mol^{-1}).

3. The methyl radicals formed then react with Cl_2 molecule forming chlorine radicals, Cl•, thus resulting in a chain reaction, since the Cl• radicals can react as in step 2, above ...

$$\bullet\text{CH}_3 + \text{Cl} \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}\bullet$$

4. There are three possible chain-terminating reactions which may bring the chain to an end ...

$$2\ \text{Cl}\bullet \longrightarrow \text{Cl}_2$$
$$2\ \text{CH}_3\bullet \longrightarrow \text{CH}_3 - \text{CH}_3$$
$$\text{Cl}\bullet + \text{CH}_3\bullet \longrightarrow \text{CH}_3\text{Cl}$$

Some ethane can be detected in the product.

5. Further Cl atoms can be introduced via Step3 giving rise to the chain:

$$\text{CH}_3\text{Cl} + \text{Cl}\bullet \longrightarrow \text{HCl} + \bullet\text{CH}_2\text{Cl}$$
$$\bullet\text{CH}_2\text{Cl} + \text{Cl}_2 \longrightarrow \text{CH}_2\text{Cl}_2 + \text{Cl}\bullet$$

Dichloromethane, CH_2Cl_2 can undergo further chlorination until all the hydrogens are substituted to form trichloromethane, (chloroform),$CHCl_3$ and CCl_4.

Thus, the chlorination of methane involves a chain reaction, consisting of three steps: initiation, propagation, and termination.

The rate of the halogenation reaction is: $F_2 > Cl_2 > Br_2 > I_2$
The reason for this is that the reaction where energy is released, i.e. in Step 2, in the making of the H — X bond, this reaction becomes more endothermic for bromination than for chlorination, hence overall energy released is less, making bromination slower than chlorination. Iodination is slow and reversible, however fluorination is dangerously explosive.

Chain reactions are or very little practical importance because a mixture of products is obtained.

(Note: methane is in our gas supply, $Cl_{2(g)}$ is used to purify and kill organisms in our drinking water; what problems could arise in our water purification plants if organic matter were to get into it?)

Extension:

Anaesthetics are substances that induce loss of sensation so that pain cannot be felt. Many fairly unreactive gases have anaesthetics properties. They are believed to work by being absorbed into the fatty tissue that surrounds nerve endings and interfering with the transmission of sensations by the nerves. Chlorinated derivatives of methane show an interesting pattern in effectiveness and toxicity:

CH_2Cl_2 $CHCl_3$ CCl_4
---------- better anaesthetics ------- >
---------------- - more toxic ---- ------>

The ideal anaesthetic should be potent, non-toxic, non-flammable and volatile enough to be administered to patients by the usual breathing apparatus used in operating theaters. The compound 1-bromo-1-chloro-2,2,2-trifluoroethane has an ideal combination of properties; and is sold under the trade name Fluothane.

Assignment

1. Calculate the lowest frequency of ultraviolet light which has enough energy to break a Cl – Cl bond (Bond energy = 243 kJmol^{-1})

2. A hydrocarbon contains 85.7 % carbon and 14.3 % hydrogen and has a relative molecular mass of 56.
   (a) what is the empirical formula?
   (b) what is its molecular formula?
   (c) The hydrocarbon does not decolorize bromine in an inert solvent. What is its structure?

3. An organic compound has the following composition by mass:
   Hydrogen: 4.1 % Carbon: 24.2 % Chlorine: 71.7 %
   (a) Calculate the empirical formula of the compound.
   (b) The mass spectrum of the compound showed the molecular ion peak at a mass/charge ratio of 98. Suggest a structural formula for the compound.

4. (a) Explain the terms: photochemical substitution, initiation step, propagation step, and termination step.
   (b) Including an equation, define standard enthalpy change of formation of chloromethane.
   (c) Given the standard enthalpy changes of formation below, calculate the enthalpy change for the overall reaction:

$$CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$$

HCl	- 72 kJ mol^{-1}
CH_4	- 75 kJ mol^{-1}
CH_3Cl	- 82 kJ mol^{-1}