

Alkanes:

Alkanes are the hydrocarbons in which all the carbon-carbon bonds are single bonds.

Some of the unbranched alkanes are listed in the table:

Name	No of Carbon atoms	Structure
Methane	1	CH_4
Ethane	2	CH_3CH_3
Propane	3	$\text{CH}_3\text{CH}_2\text{CH}_3$
Butane	4	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$
Pentane	5	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$
Hexane	6	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
Heptane	7	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$
Octane	8	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
Nonane	9	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$
Decane	10	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$
Undecane	11	$\text{CH}_3(\text{CH}_2)_9\text{CH}_3$
Dodecane	12	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$
Tridecane	13	$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_3$
Tetradecane	14	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$
Nonadecane	19	$\text{CH}_3(\text{CH}_2)_{17}\text{CH}_3$
Eicosane	20	$\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$
Heneicosane	21	$\text{CH}_3(\text{CH}_2)_{19}\text{CH}_3$
Docosane	22	$\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$
Tricosane	23	$\text{CH}_3(\text{CH}_2)_{21}\text{CH}_3$
Triacontane	30	$\text{CH}_3(\text{CH}_2)_{28}\text{CH}_3$
Tetracontane	40	$\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$
Pentacontane	50	$\text{CH}_3(\text{CH}_2)_{48}\text{CH}_3$
Nonacontane	90	$\text{CH}_3(\text{CH}_2)_{88}\text{CH}_3$
Hectane	100	$\text{CH}_3(\text{CH}_2)_{98}\text{CH}_3$

Chemical Reactivity of Alkanes:

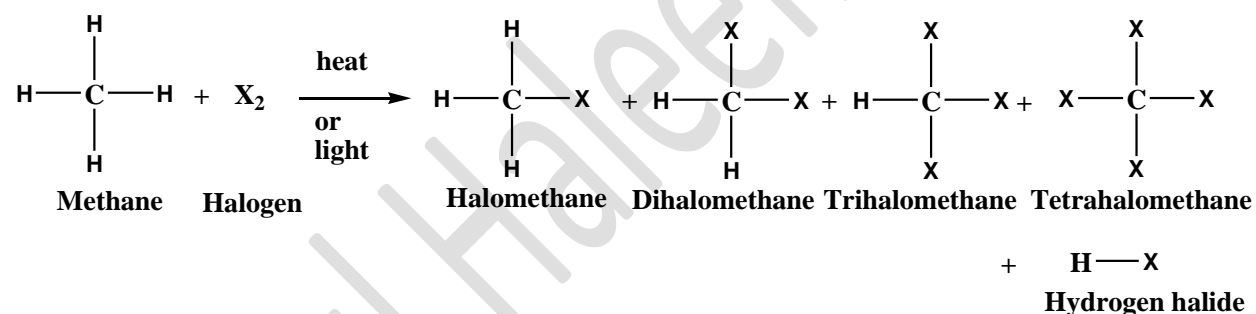
Alkanes, as a class, are characterized by a general inertness to many chemical reactions. The reasons for this inertness include the strength of C-H and C-C bonds and very small polarization of C-H bond. The C-C and C-H bonds are quite strong; they do not break unless alkanes are heated to very high temperatures. Since Carbon and Hydrogen have nearly the same electronegativity, the C-H bond is only slightly polarized. As a result of this, alkanes are generally unaffected by most

bases. Alkanes are inert to acids as well, as they have no unshared electrons to offer sites of attack by acids. Because of this inertness, alkanes were originally called *paraffins* (Latin: *parum affinis*, little affinity).

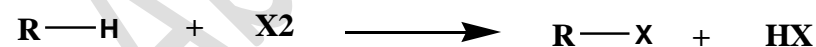
The term paraffin is however not appropriate. Alkanes do react with Oxygen when an appropriate mixture is ignited. This combustion occurs in the cylinders of automobiles and oil furnaces. When heated, alkanes also react with Chlorine and Bromine, and they also react explosively with Fluorine.

The Reactions of Alkanes with Halogens:

Methane, Ethane and other alkanes react with the first three members of the Halogen family: Fluorine, Chlorine and Bromine. Alkanes do not react appreciably with Iodine. With Methane the reaction produces a mixture of halomethanes and hydrogen halide.



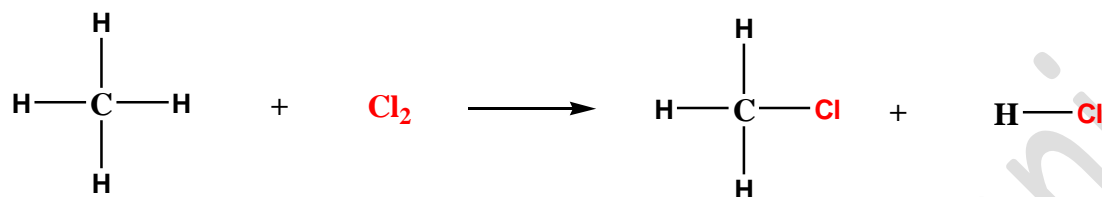
This reaction called halogenation is a substitution reaction in which a halogen atom replaces one of the hydrogen atoms of alkane. The general reaction to produce monohaloalkane can be written as follows:



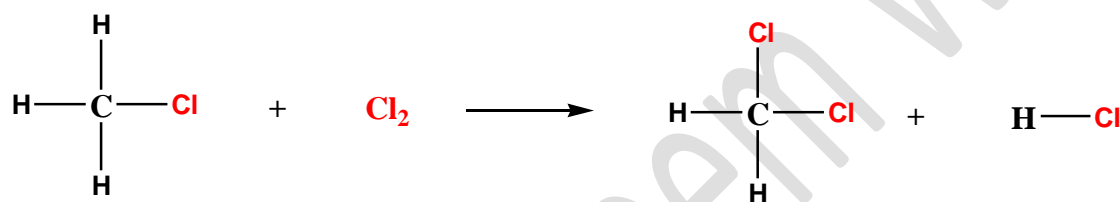
Multiple Substitution Reactions and Selectivity

One of the disadvantages of the alkane halogenation is that multiple substitutions always often occur. As we have seen that upon halogenation, ethane produces a mixture of monohalomethane, dihalomethane, trihalomethane and tetrahalomethane. This happens because all hydrogens attached to the carbon are able to react with halogens.

Let us consider reaction between methane and chlorine as an example. A vigorous reaction occurs when a mixture of methane and chlorine is either heated or irradiated with light. Since at the beginning only chlorine and methane are present in the reaction mixture, the only reaction that can take place is the one that produces chloromethane and hydrogen chloride.



As the reaction progresses, the concentration of chloromethane increases. Chloromethane now reacts with chlorine to produce dichloromethane in a second substitution reaction.

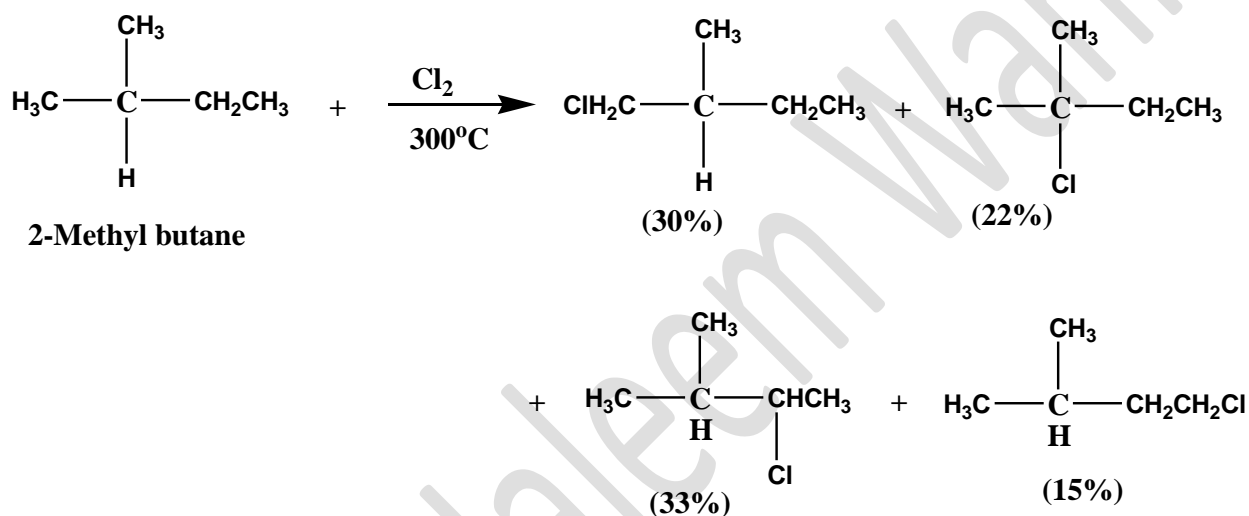
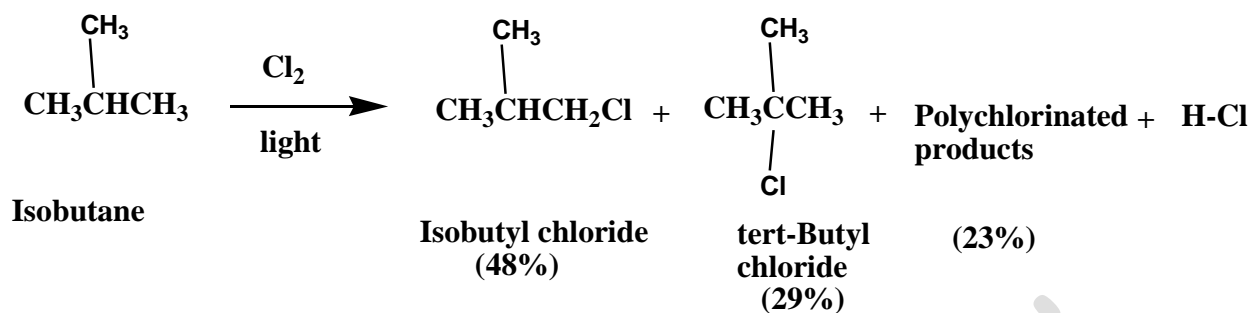


The dichloromethane reacts further to produce trichloromethane, which in turn reacts further to produce tetrachloromethane. Each time a chlorine substitutes a hydrogen, a molecule of hydrogen chloride is produced.

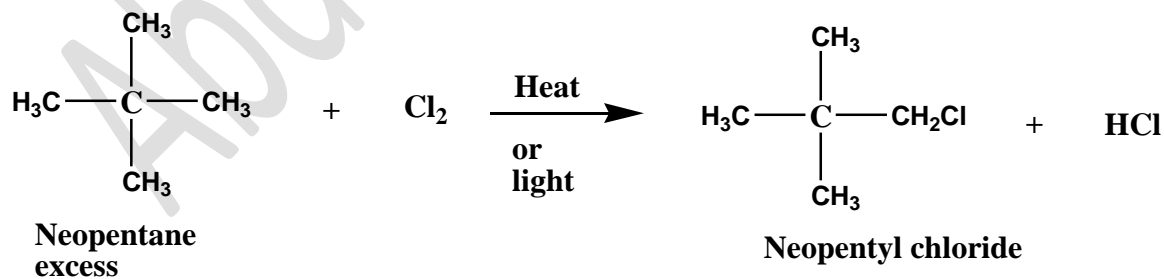
Can we maximize the formation of monochlorination product?

The use of large excess of methane maximizes the probability that chlorine will attack methane molecules because of their relatively high concentration. It also minimizes the probability of attack of chlorine on CH₃Cl, CH₂Cl, and CHCl₃ because of their relatively low concentrations.

Chlorination of most higher alkanes gives a mixture of isomeric monochloro products as well as more highly halogenated products. Chlorine is relatively **unselective** as it does not discriminate between different types of hydrogens (primary, secondary, and tertiary) in an alkane. For example:

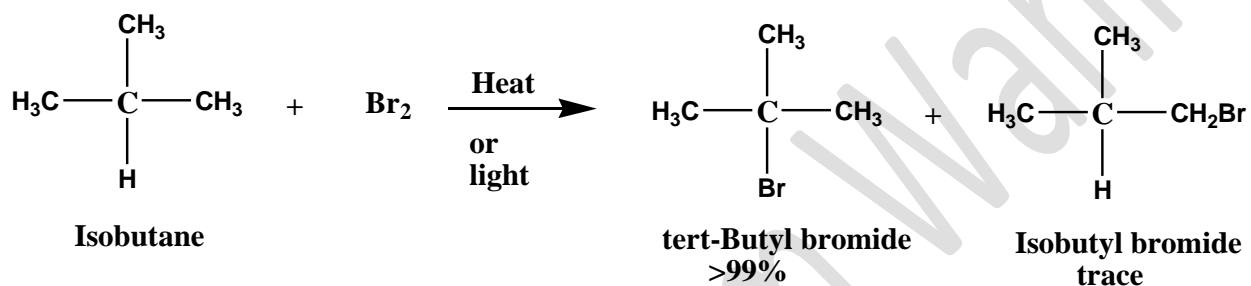


Since chlorination of alkanes produces a mixture of compounds, these reactions have no great synthetic importance. Halogenation of an alkane can lead to a single product if all its hydrogens are equivalent. Neopentane, for example, can form only one monohalogenation product and use of a large excess of neopentane minimizes polychlorination.



Selectivity of Bromine:

Bromine is less reactive towards alkanes in general than chlorine, but bromine is more selective in choosing the site of attack. Bromine shows a much greater ability to discriminate between different types of hydrogen atoms. The reaction of isobutene and bromine produces *tert*-butyl bromide as exclusive product (replacement of tertiary hydrogen atom).



Fluorine being much more reactive than chlorine, is even less selective than chlorine. In fact, there is a little difference in the rate at which 1°, 2° and 3° hydrogens react with fluorine. Iodine is so less reactive that for all practical purposes we can say that no reaction takes place.