4.15

Halogenation of Alkanes

$$RH + X_2 \varnothing RX + HX$$

Energetics

$$\mathrm{RH} + \mathrm{X}_2 \ \varnothing \ \mathrm{RX} + \mathrm{HX}$$

explosive for F_2

exothermic for Cl_2 and Br_2

endothermic for I_2

4.16

Chlorination of Methane

Chlorination of Methane

carried out at high temperature (400 °C)

$CH_4 + Cl_2 \varnothing CH_3Cl + HCl$

$CH_3Cl + Cl_2 \varnothing CH_2Cl_2 + HCl$

$CH_2Cl_2 + Cl_2 \varnothing CHCl_3 + HCl$

$CHCl_3 + Cl_2 \varnothing CCl_4 + HCl$

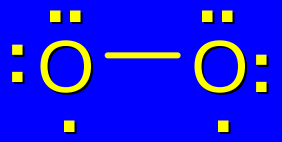
4.17

Structure and Stability of Free Radicals

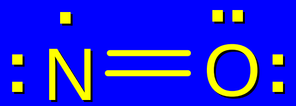
Free Radicals

contain unpaired electrons

Examples: O_2

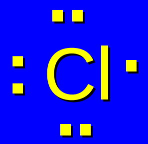


NO

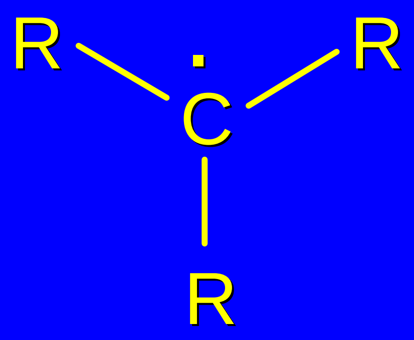


Li $1s^2\ 2s^1$

Cl



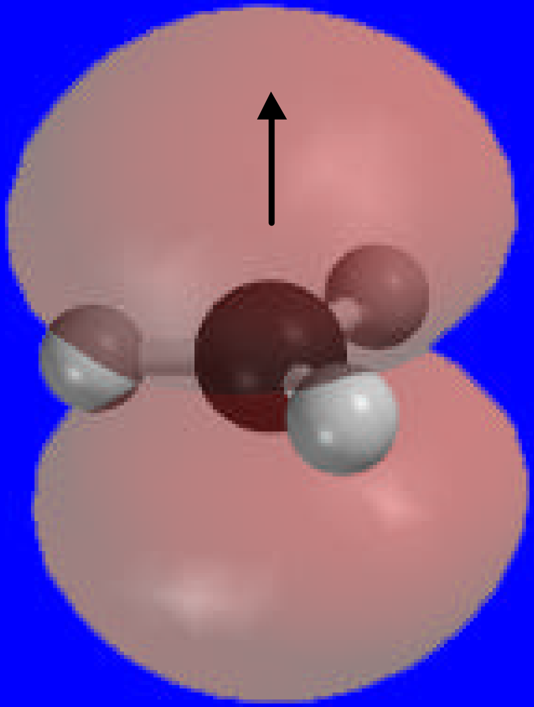
Alkyl Radicals



Most free radicals in which carbon bears the unpaired electron are too unstable to be isolated.

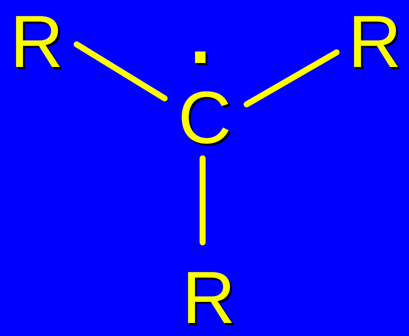
Alkyl radicals are classified as primary, secondary, or tertiary in the same way that carbocations are.

Figure 4.15 Structure of methyl radical.



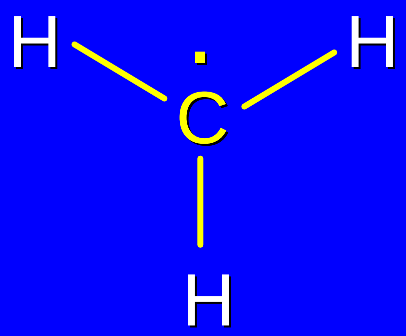
Methyl radical is planar, which suggests that carbon is *sp*^{2} hybridized and that the unpaired electron is in a *p* orbital.

Alkyl Radicals

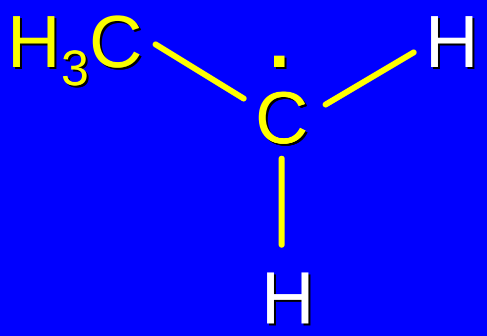


The order of stability of free radicals is the same as for carbocations.

Alkyl Radicals



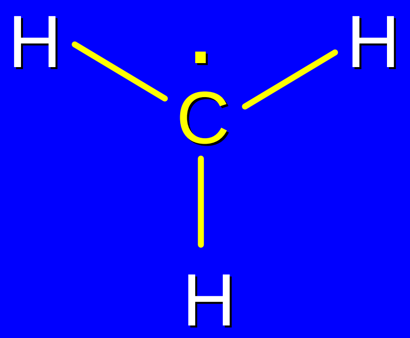
less stable than



Methyl radical

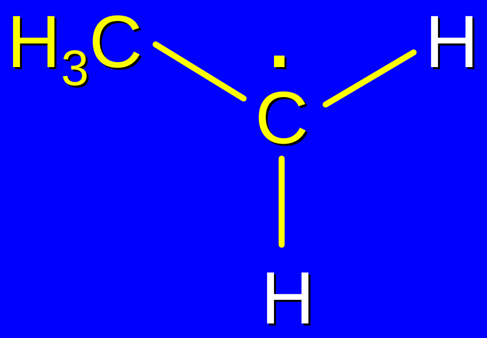
Ethyl radical
(primary)

Alkyl Radicals



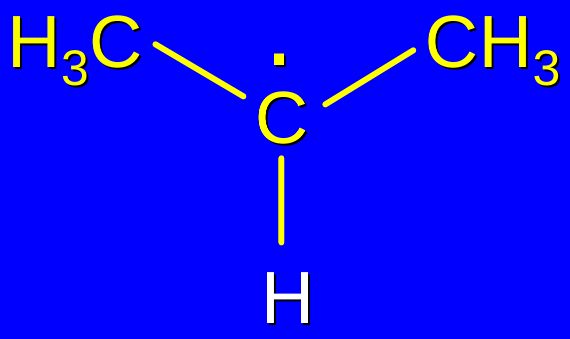
Methyl radical

less stable
than



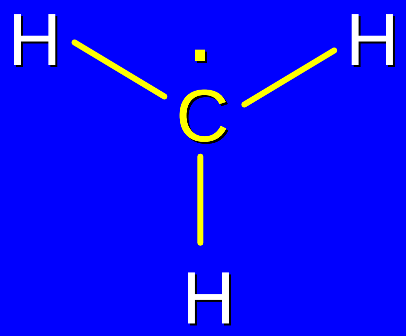
Ethyl radical
(primary)

less stable
than



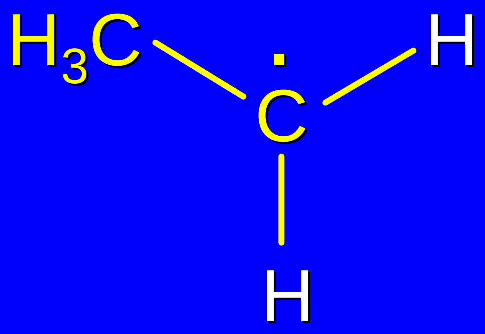
Isopropyl radical
(secondary)

Alkyl Radicals



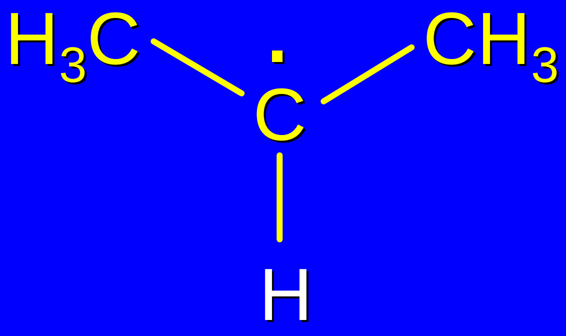
Methyl radical

less stable than



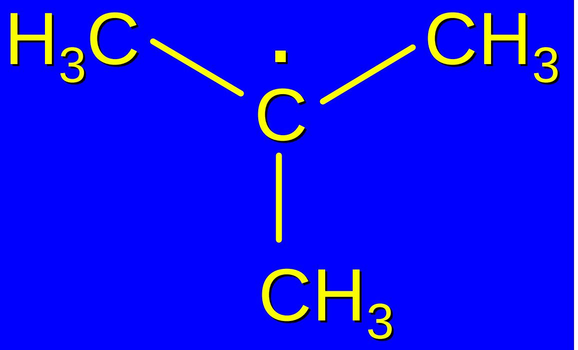
Ethyl radical
(primary)

less stable than



Isopropyl radical
(secondary)

less stable than



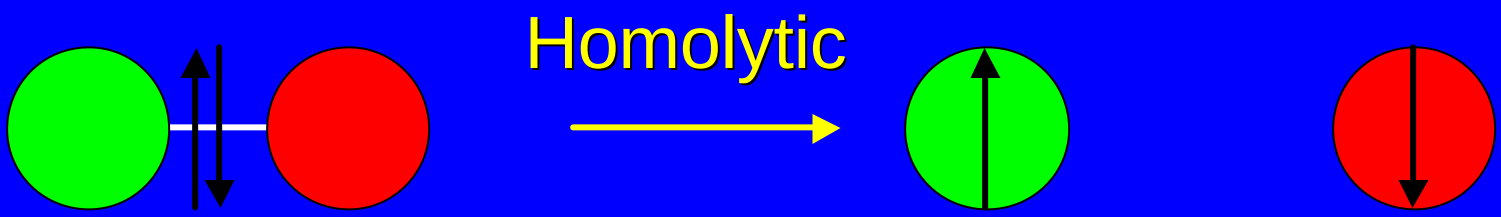
tert-Butyl radical
(tertiary)

Alkyl Radicals

The order of stability of free radicals can be determined by measuring bond strengths.

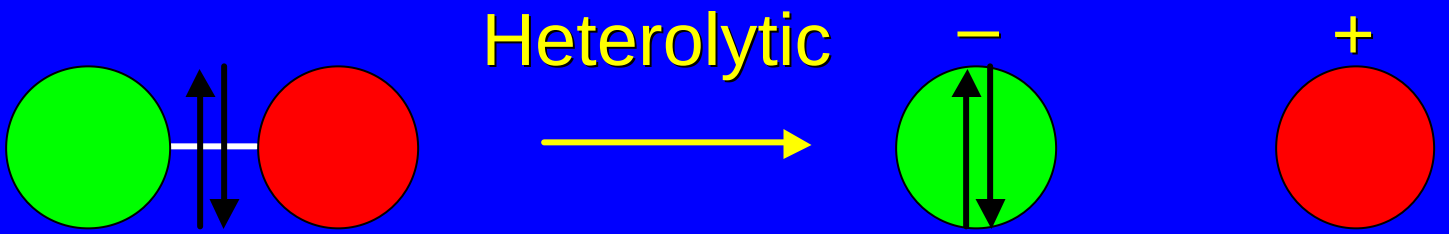
By "bond strength" we mean the energy required to break a covalent bond.

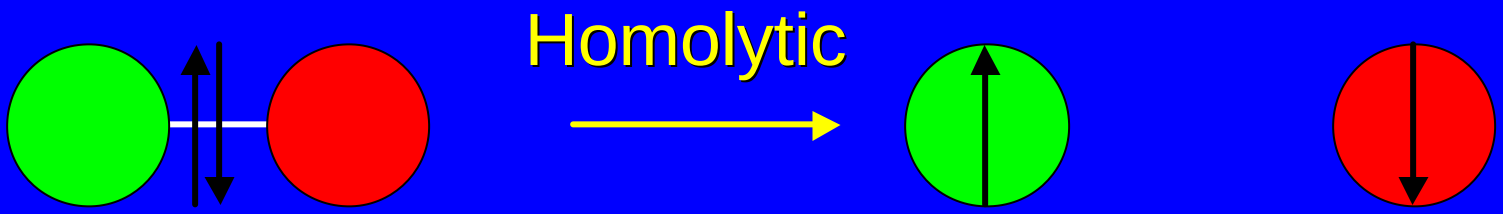
A chemical bond can be broken in two different ways—heterolytically or homolytically.



In a homolytic bond cleavage, the two electrons in the bond are divided equally between the two atoms. One electron goes with one atom, the second with the other atom.

In a heterolytic cleavage, one atom retains both electrons.



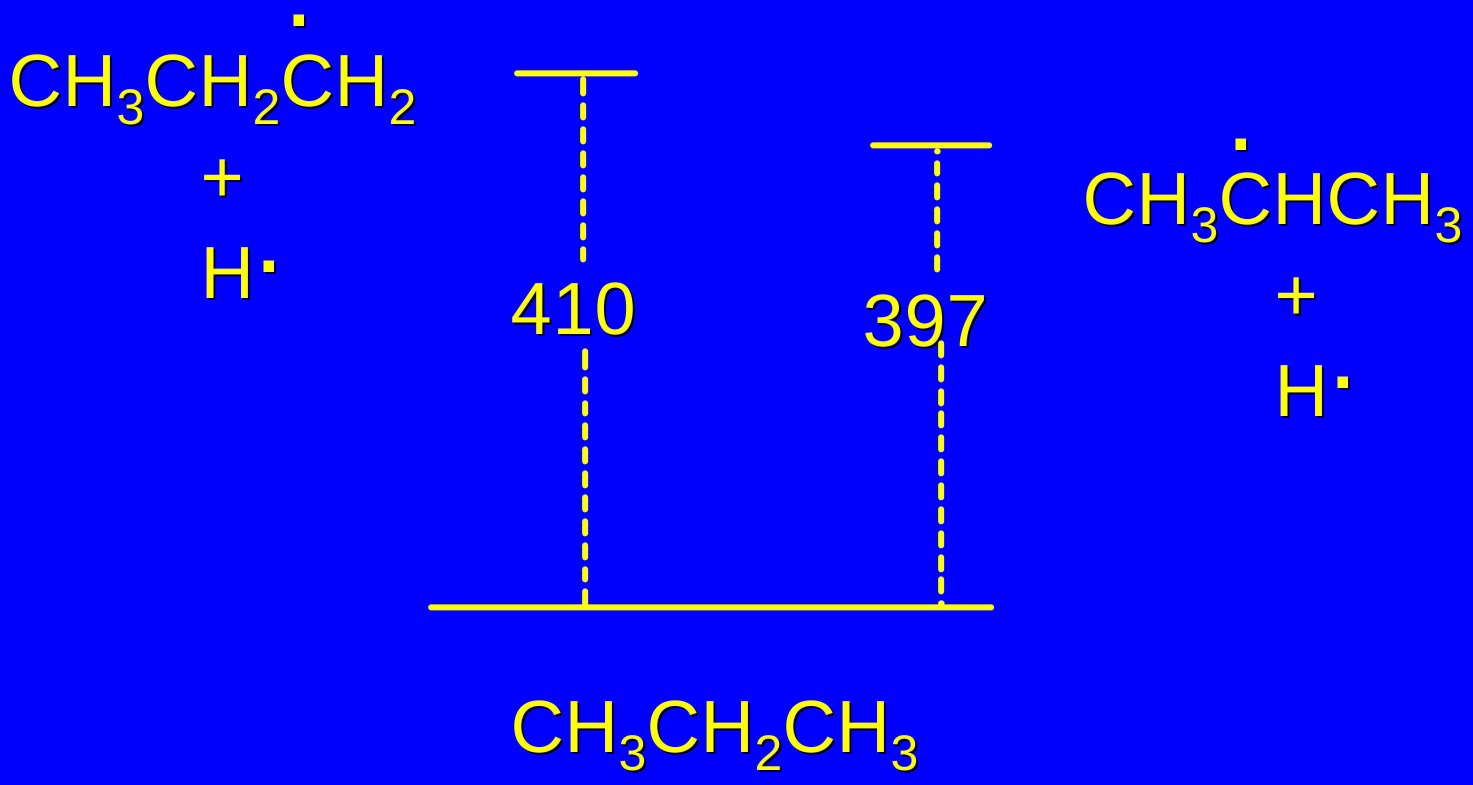


The species formed by a homolytic bond cleavage of a neutral molecule are free radicals. Therefore, measure energy cost of homolytic bond cleavage to gain information about stability of free radicals.

The more stable the free-radical products, the weaker the bond, and the lower the bond-dissociation energy.

Measures of Free Radical Stability

Bond-dissociation energy measurements tell us that isopropyl radical is 13 kJ/mol more stable than propyl.



$CH_3CH_2\dot{C}H_2$

+

$H\cdot$

410

397

$CH_3\dot{C}HCH_3$

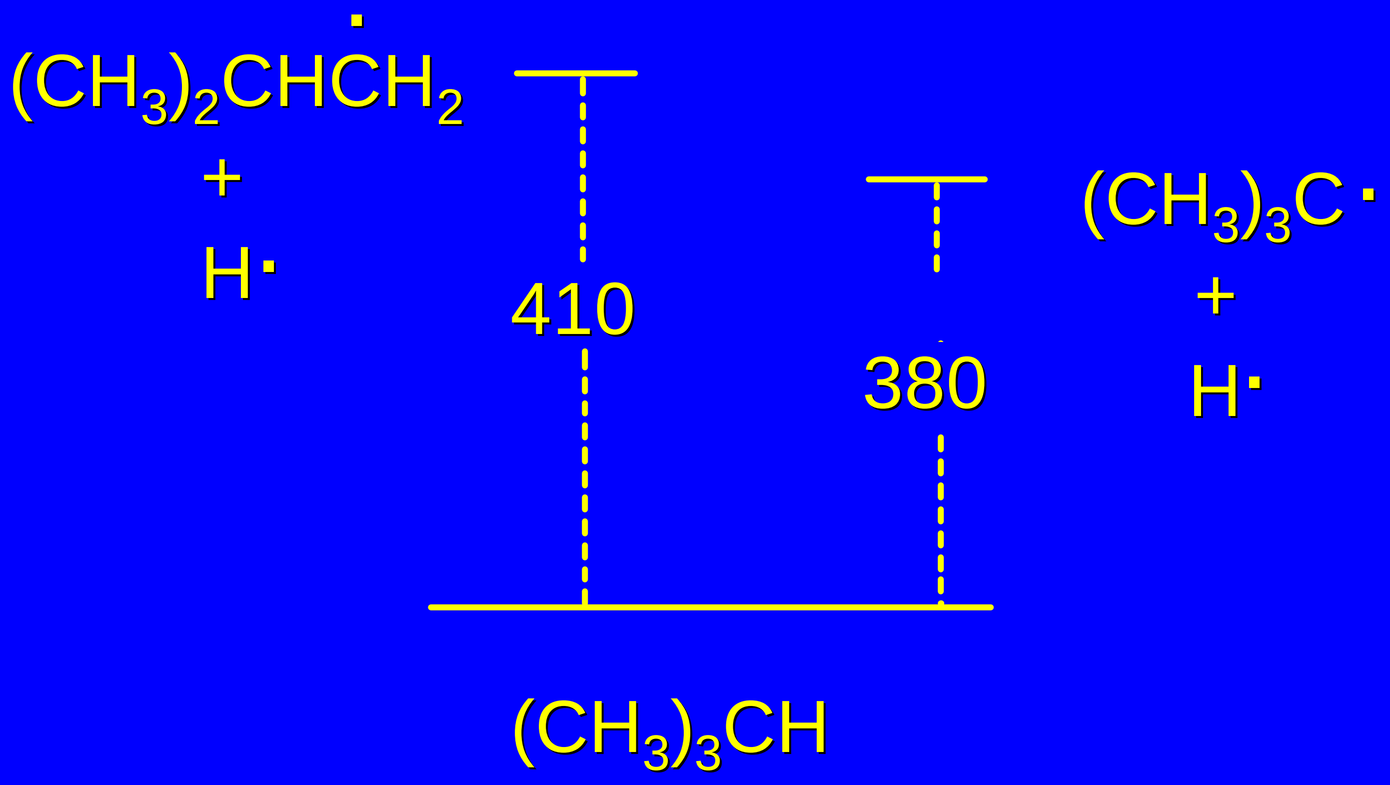
+

$H\cdot$

$CH_3CH_2CH_3$

Measures of Free Radical Stability

Bond-dissociation energy measurements tell us that *tert*-butyl radical is 30 kJ/mol more stable than isobutyl.



$(CH_3)_2CH\dot{C}H_2$

+

$H\cdot$

410

380

$(CH_3)_3C\cdot$

+

$H\cdot$

$(CH_3)_3CH$

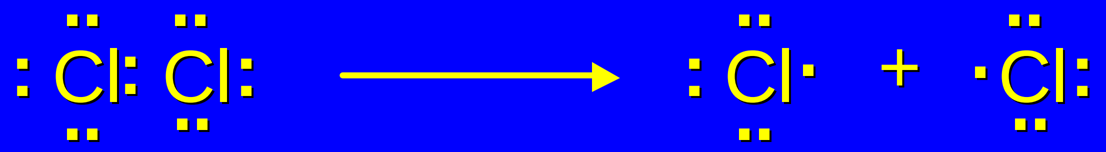
4.18

Mechanism of Chlorination of Methane

Mechanism of Chlorination of Methane

Free-radical chain mechanism.

Initiation step:



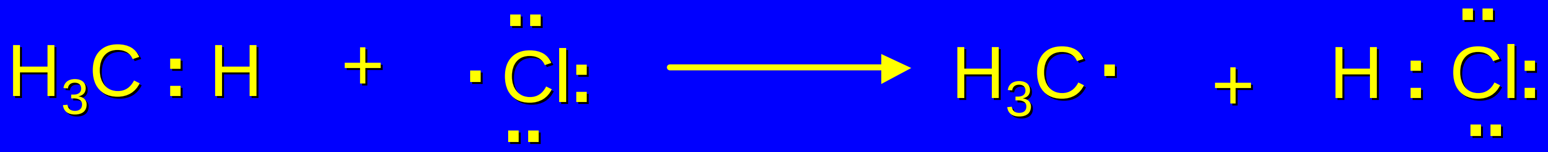
$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$$

The initiation step "gets the reaction going" by producing free radicals—chlorine atoms from chlorine molecules in this case.

Initiation step is followed by propagation steps. Each propagation step consumes one free radical but generates another one.

Mechanism of Chlorination of Methane

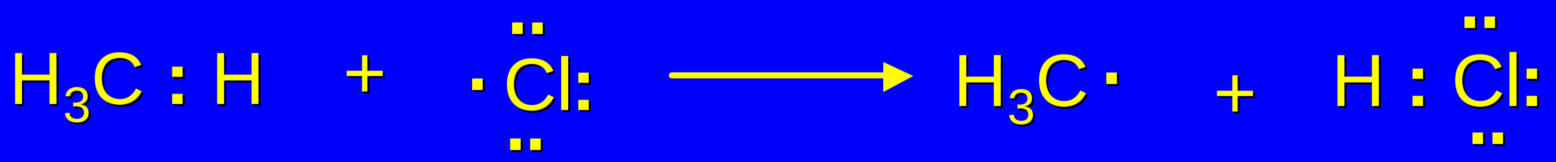
First propagation step:



$$H_3C : H + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \longrightarrow H_3C\cdot + H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

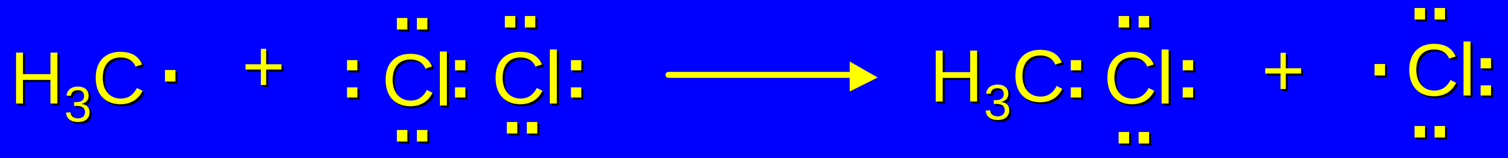
Mechanism of Chlorination of Methane

First propagation step:



$$H_3C : H \; + \; \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \longrightarrow H_3C\cdot \; + \; H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

Second propagation step:



$$H_3C\cdot \; + \; :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \longrightarrow H_3C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \; + \; \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

Mechanism of Chlorination of Methane

First propagation step:

$$H_3C : H \quad + \quad \cancel{\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:} \longrightarrow \cancel{H_3C\,\cdot} \quad + \quad H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

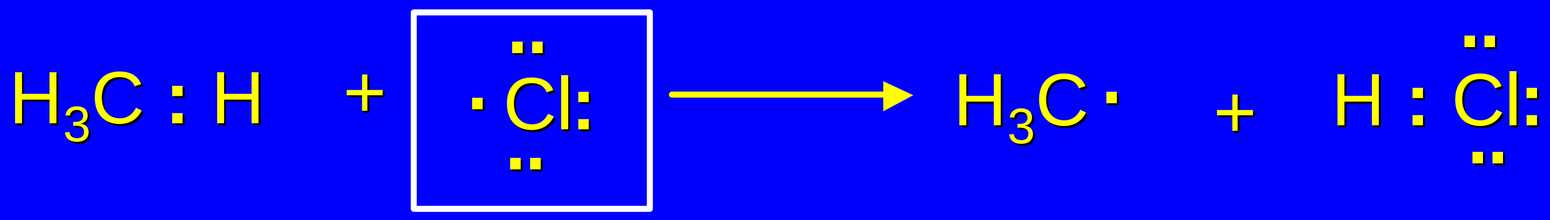
Second propagation step:

$$\cancel{H_3C\,\cdot} \quad + \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow H_3C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \quad + \quad \cancel{\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:}$$

$$H_3C : H \quad + \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow H_3C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \quad + \quad H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

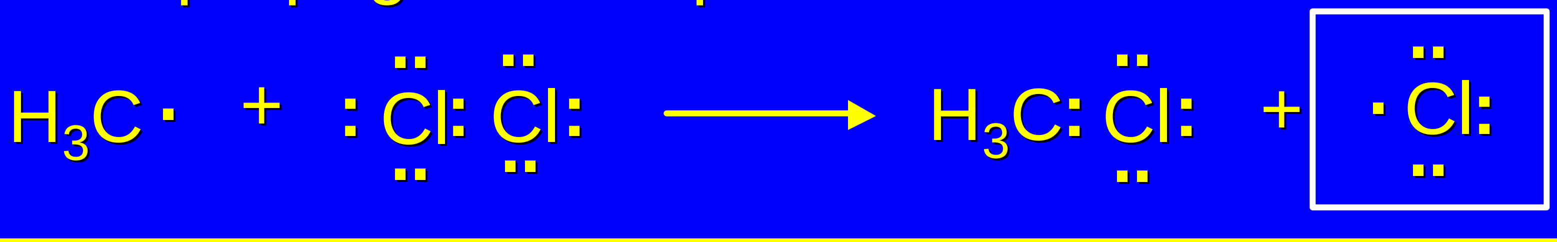
Almost all of the product is formed by repetitive cycles of the two propagation steps.

First propagation step:

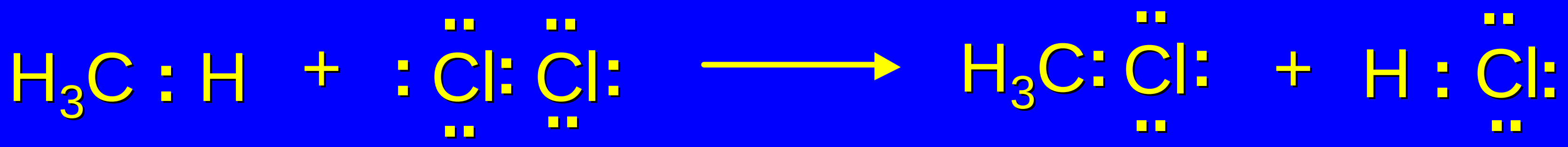


$$H_3C:H + \boxed{\cdot\overset{..}{\underset{..}{Cl}}:} \longrightarrow H_3C\cdot + H:\overset{..}{\underset{..}{Cl}}:$$

Second propagation step:



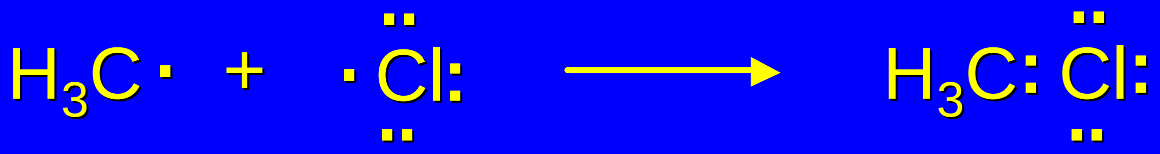
$$H_3C\cdot + :\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}: \longrightarrow H_3C:\overset{..}{\underset{..}{Cl}}: + \boxed{\cdot\overset{..}{\underset{..}{Cl}}:}$$



$$H_3C:H + :\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}: \longrightarrow H_3C:\overset{..}{\underset{..}{Cl}}: + H:\overset{..}{\underset{..}{Cl}}:$$

Termination Steps

stop chain reaction by consuming free radicals



$$H_3C\cdot \;+\; \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\!: \longrightarrow H_3C\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\!:$$

hardly any product is formed by termination step because concentration of free radicals at any instant is extremely low

4.19

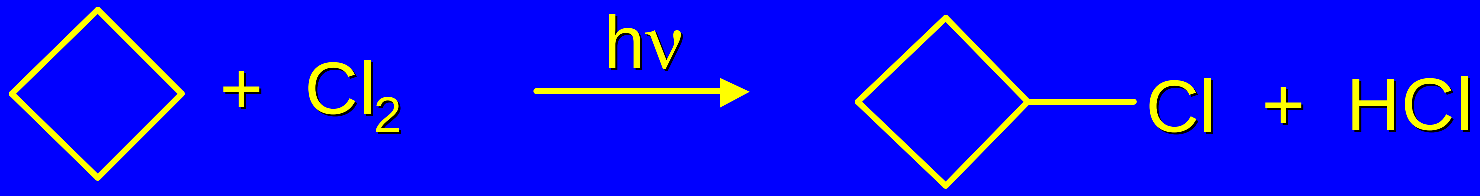
Halogenation of Higher Alkanes

Chlorination of Alkanes

can be used to prepare alkyl chlorides from alkanes in which all of the hydrogens are equivalent to one another

$$\mathrm{CH_3CH_3 + Cl_2 \xrightarrow{420^\circ C} CH_3CH_2Cl + HCl}$$

(78%)



(73%)

Chlorination of Alkanes

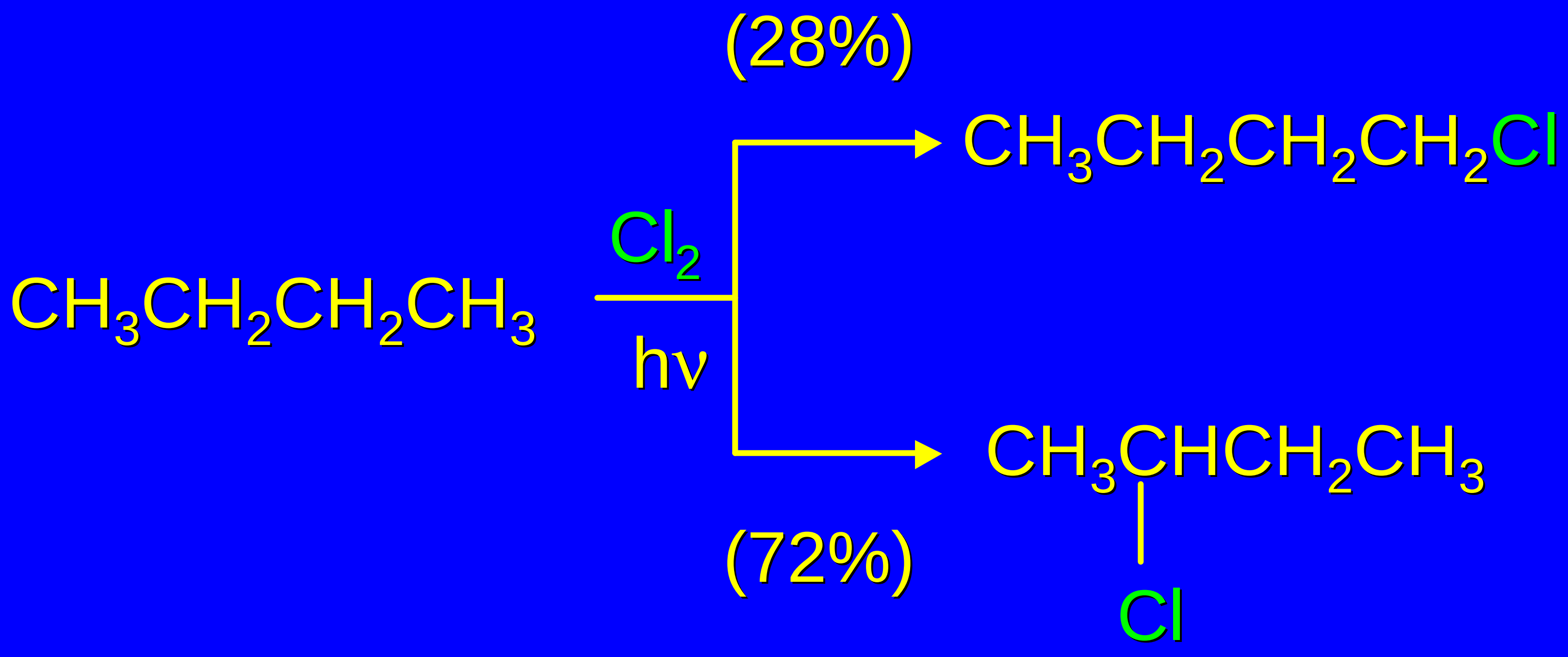
Major limitation:

Chlorination gives every possible monochloride derived from original carbon skeleton.

Not much difference in reactivity of different hydrogens in molecule.

Example

Chlorination of butane gives a mixture of 1-chlorobutane and 2-chlorobutane.

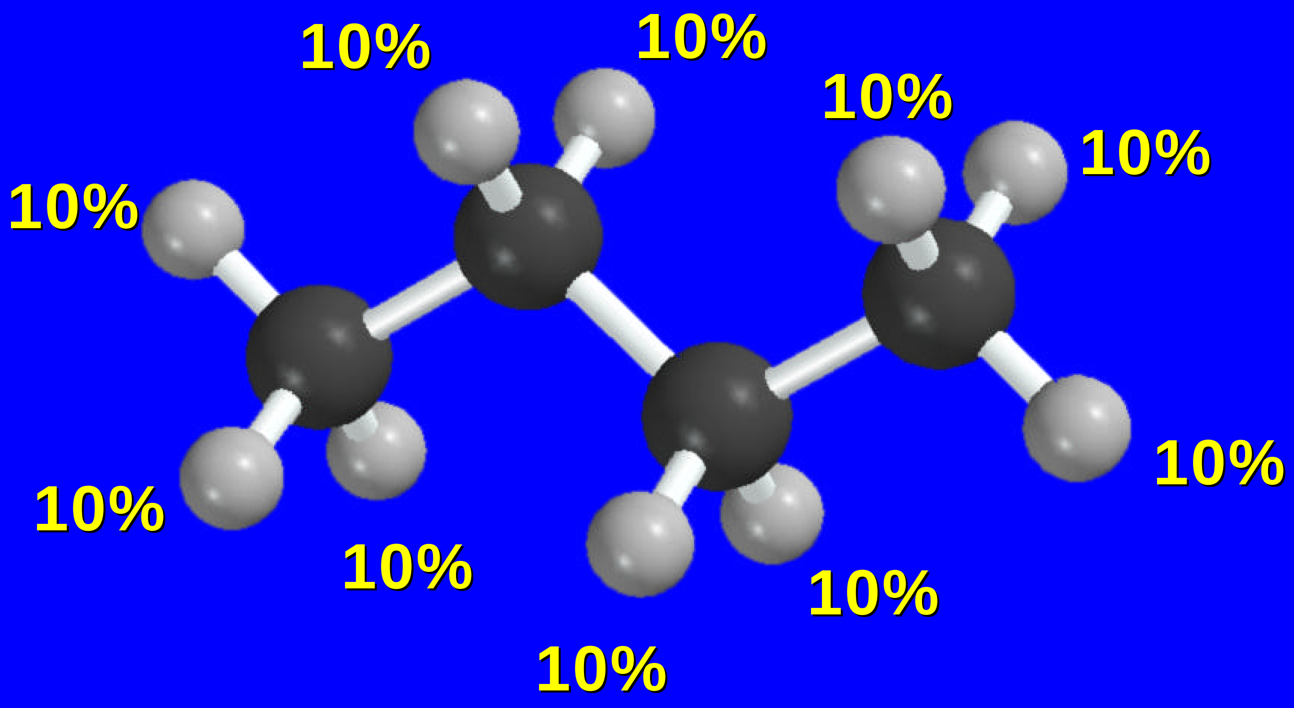


$CH_3CH_2CH_2CH_3 \xrightarrow[h\nu]{Cl_2}$

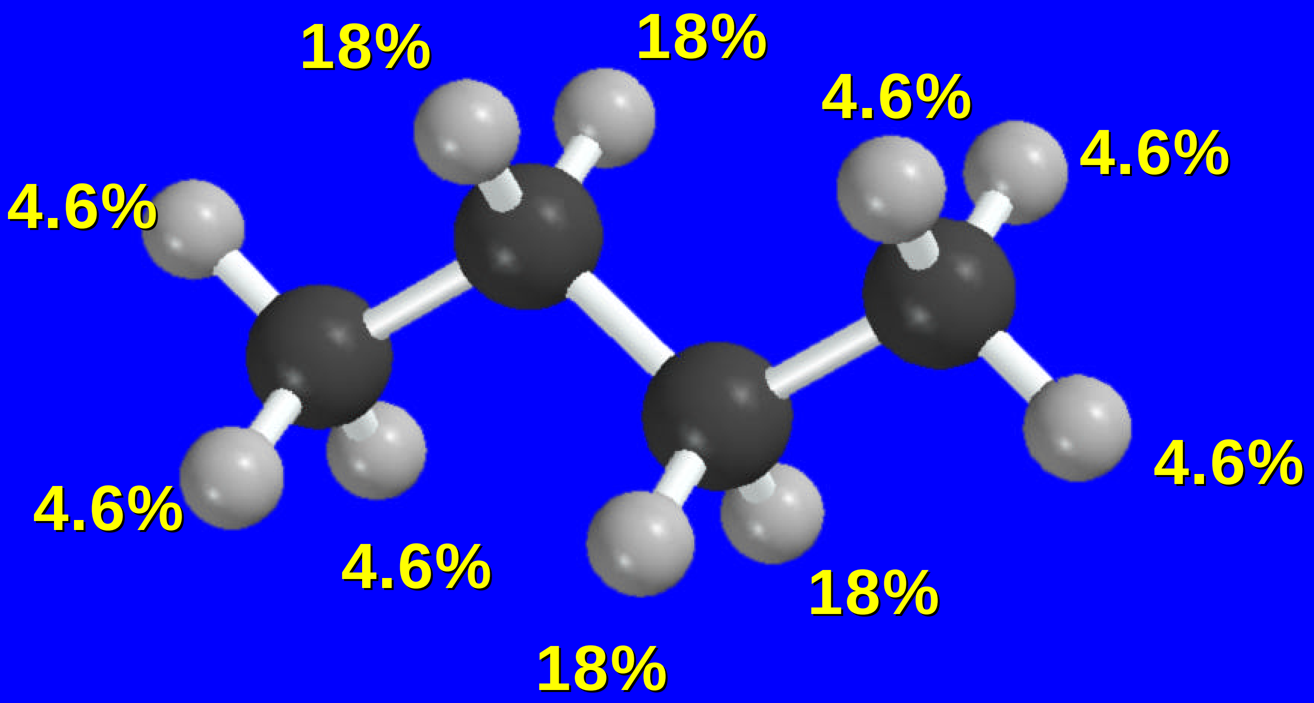
(28%) $CH_3CH_2CH_2CH_2Cl$

(72%) $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3$

Percentage of product that results from substitution of indicated hydrogen if every collision with chlorine atoms is productive



Percentage of product that actually results from replacement of indicated hydrogen

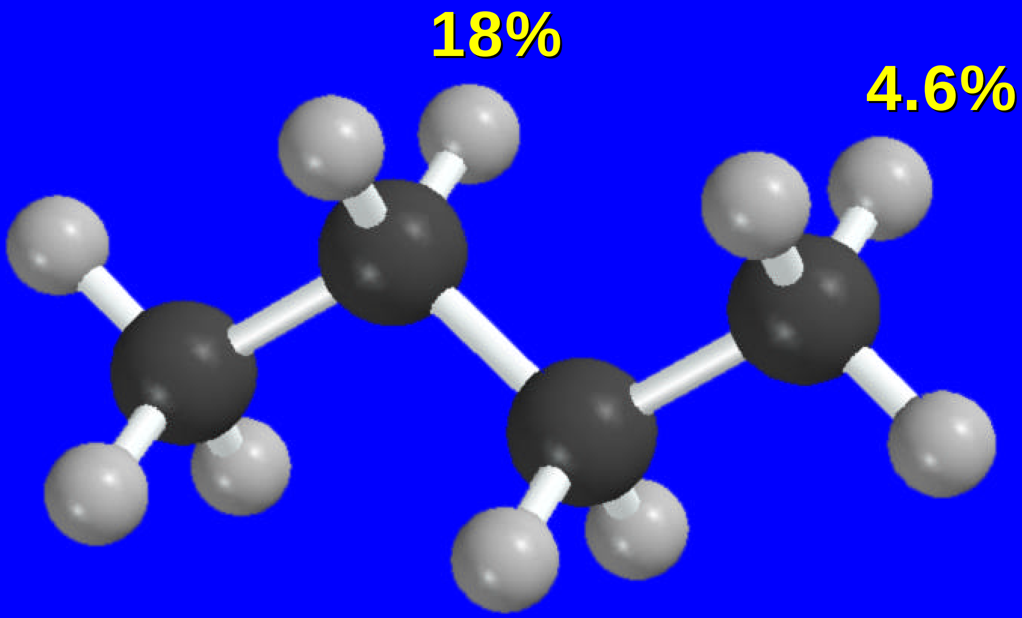


Relative rates of hydrogen atom abstraction

divide by 4.6

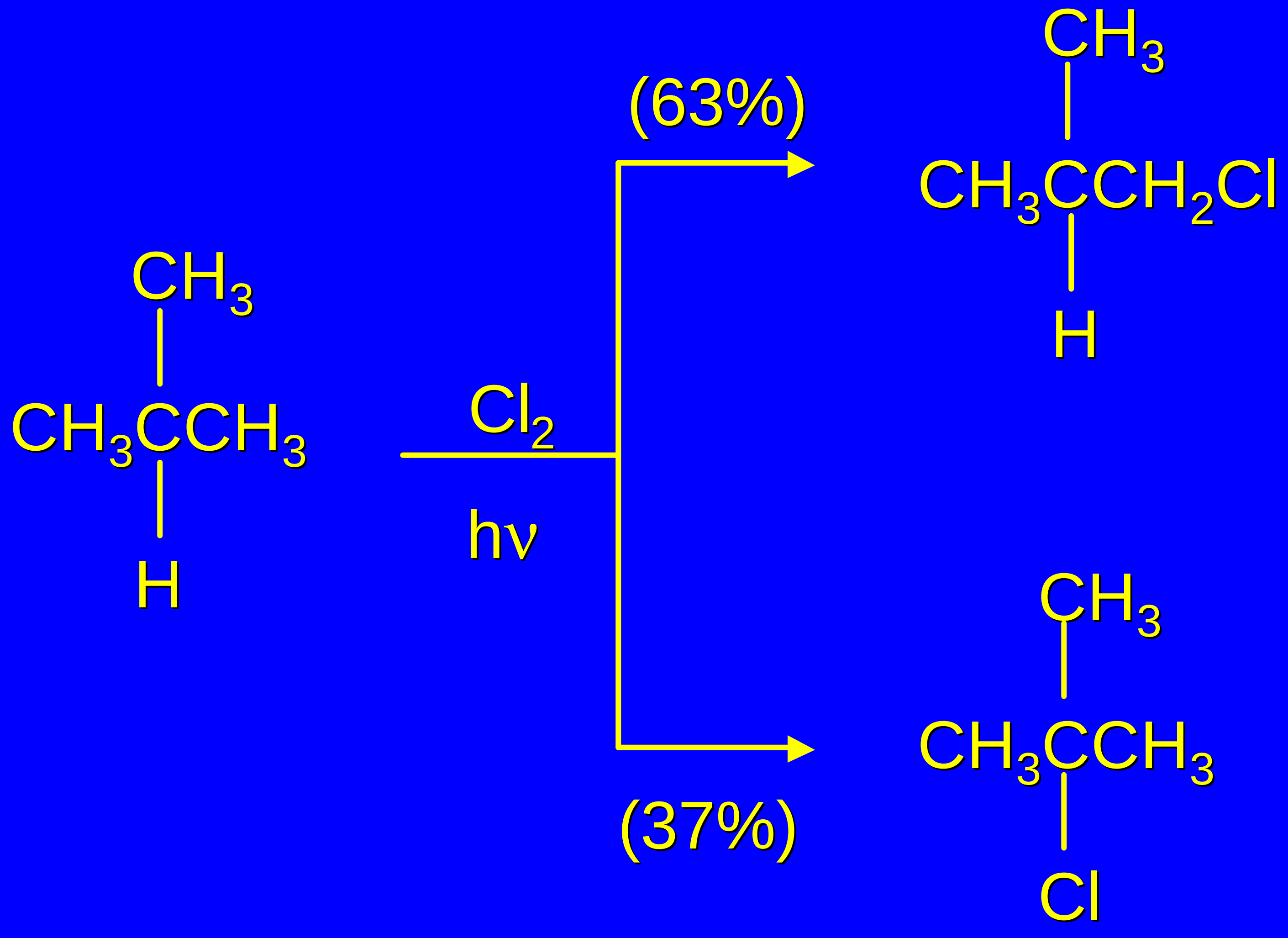
$$\frac{4.6}{4.6} = 1$$

$$\frac{18}{4.6} = 3.9$$



A <u>secondary</u> hydrogen is abstracted 3.9 times faster than a <u>primary</u> hydrogen by a chlorine atom.

Similarly, chlorination of 2-methylbutane gives a mixture of isobutyl chloride and tert-butyl chloride



$$CH_3\underset{H}{\overset{CH_3}{C}}CH_3 \xrightarrow[h\nu]{Cl_2}$$

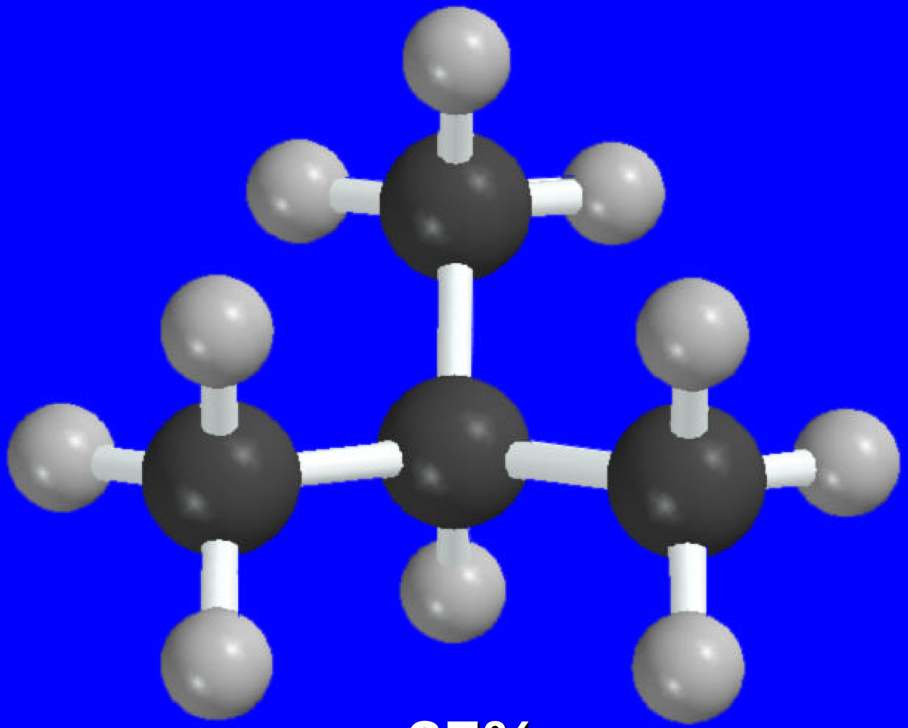
(63%)

$$CH_3\underset{H}{\overset{CH_3}{C}}CH_2Cl$$

(37%)

$$CH_3\underset{Cl}{\overset{CH_3}{C}}CH_3$$

Percentage of product that results from replacement of indicated hydrogen



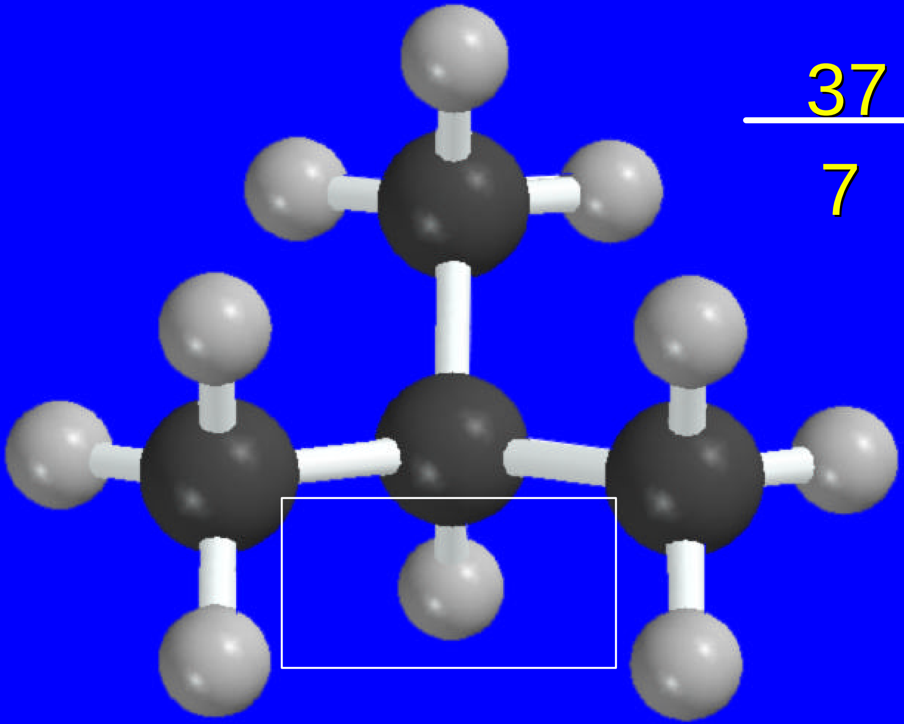
7.0%

37%

Relative rates of hydrogen atom abstraction

divide by 7

$\frac{7.0}{7} = 1$



$\frac{37}{7} = 5.3$

A <u>tertiary</u> hydrogen is abstracted 5.3 times faster than a <u>primary</u> hydrogen by a chlorine atom.

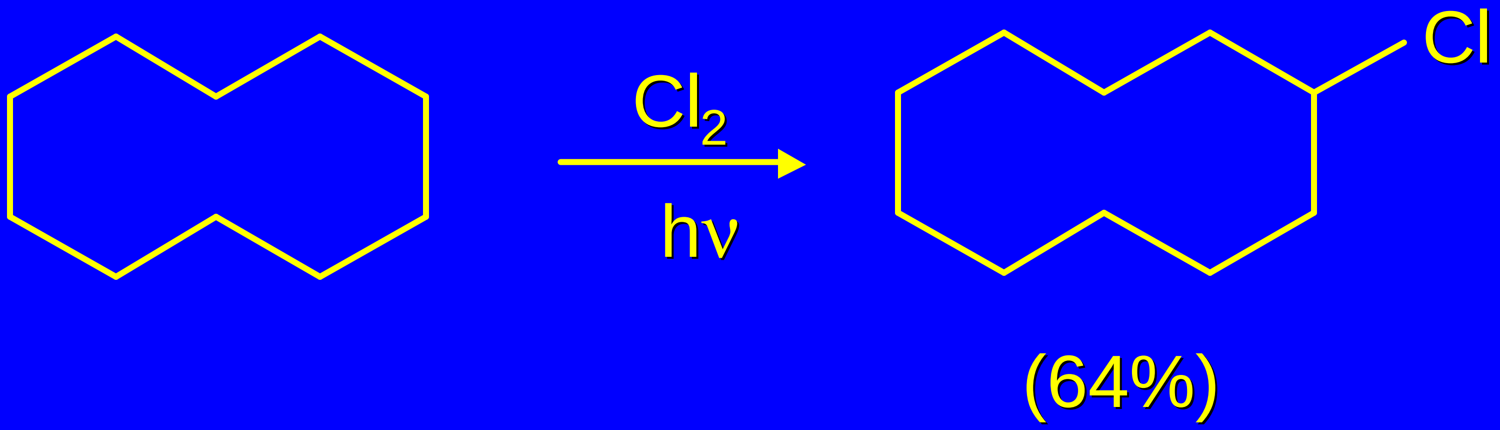
Selectivity of free-radical halogenation

	R_3CH	>	R_2CH_2	>	RCH_3
chlorination:	5		4		1
bromination:	1640		82		1

Chlorination of an alkane gives a mixture of every possible isomer having the same skeleton as the starting alkane. Useful for synthesis only when all hydrogens in a molecule are equivalent.

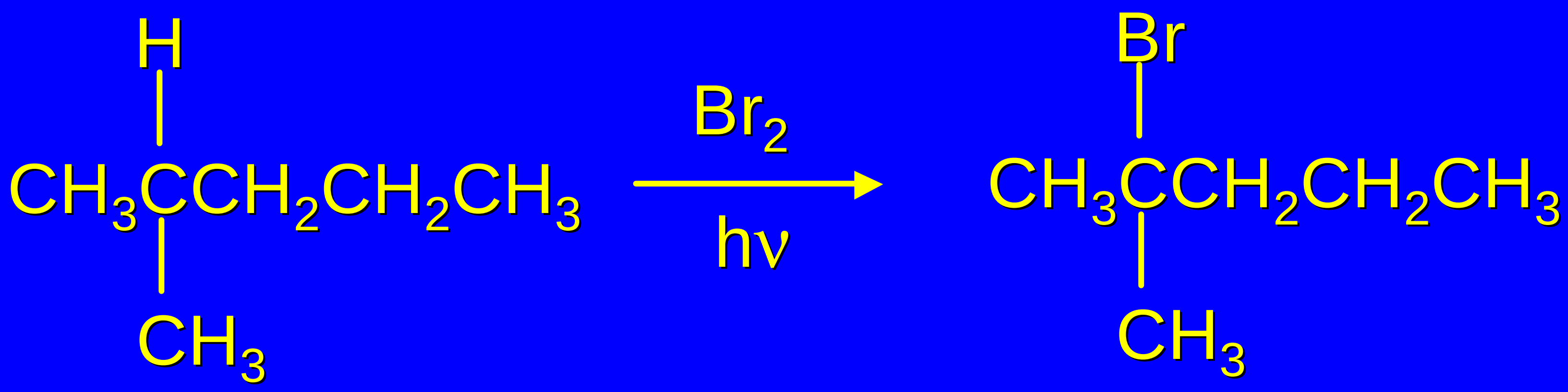
Bromination is highly regioselective for substitution of tertiary hydrogens. Major synthetic application is in synthesis of tertiary alkyl bromides.

Synthetic application of chlorination of an alkane



Chlorination is useful for synthesis only when all of the hydrogens in a molecule are equivalent.

Synthetic application of bromination of an alkane



$$\mathrm{CH_3}\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{H}\\ |}}{\mathrm{C}}}\mathrm{CH_2CH_2CH_3} \xrightarrow[h\nu]{\mathrm{Br_2}} \mathrm{CH_3}\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{\substack{\mathrm{Br}\\ |}}{\mathrm{C}}}\mathrm{CH_2CH_2CH_3}$$

(76%)

Bromination is highly selective for substitution of tertiary hydrogens.

Major synthetic application is in synthesis of tertiary alkyl bromides.