HALOGENATION OF ALKANES:

Under the influence of UV light, chlorine or Bromine converts alkane into chloroalkane / Bromoalkane.

$$CH_4 + X_2 \xrightarrow{UV} CH_3X + HX$$

(Usually mixture)

- $CH_3-CH_3 + Cl_2 \xrightarrow{UV} CH_3CH_2Cl + HCl$
- $CH_3-CH_2-CH_3 + Cl_2 \xrightarrow{UV} CH_3-CH_2-CH_2Cl + CH_3-\underset{Cl}{CH}-CH_3$

(45%) (Minor) (55%) (Major)

- $CH_3-\underset{CH_3}{CH}-CH_3 + Cl_2 \xrightarrow{UV} CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3 + CH_3-\overset{CH_3}{CH}-CH_2Cl$

(Major) (Minor)

- $CH_3-CH_3 + Br_2 \xrightarrow{UV} CH_3CH_2Br + HBr$
- $CH_3-CH_2-CH_3 + Br_2 \xrightarrow{UV} CH_3-\underset{Br}{CH}-CH_3 + CH_3-CH_2-CH_2Br + HBr$

(Major) (97%) (Minor) (3%)

- $CH_3-\underset{CH_3}{CH}-CH_3 + Br_2 \xrightarrow{UV} CH_3-\underset{Br}{\overset{CH_3}{CH}}-CH_3 + CH_3-\overset{CH_2}{CH}-CH_2Br$

(Major) (99%) (Minor) (1%)

* Chlorination gives mixture in which no isomer greatly predominates but in Bromination, one isomer predominates due to low reactivity of Bromine atom.

Low
No reactivity . more selectivity

* Mechanism of Halogenation:

Step - I $X_2 \xrightarrow{UV} 2X^{\cdot}$ (chain initiating step)

(free radicals)

Step - II $X^{\cdot} + RH \longrightarrow \dot{R} + HX$

Step - III $\dot{R} + X_2 \longrightarrow R-X + X^{\cdot}$ } (chain propagating step)

↳ Step II, III (repeats)

$CH_3-CH_2-CH_3 \xrightarrow{X^{\cdot}}$

Abstraction of primary hydrogen

$CH_3-CH_2-\dot{C}H_2 \xrightarrow{X_2} CH_3CH_2-CH_2X + X^{\cdot}$

(n-propyl radical) (n-propyl halide)

Abstraction of secondary hydrogen

$CH_3-\dot{C}H-CH_3 \xrightarrow{X_2} CH_3-\underset{X}{CH}-CH_3 + X^{\cdot}$

(Isopropyl radical) (Isopropane halide)

Rate of abstraction of Hydrogen $3^{\circ} > 2^{\circ} > 1^{\circ}$.

* Stability of free radicals: 15 C

Homolytic dissociation energies -

$CH_3-H \longrightarrow \dot{C}H_3 + \dot{H}$ ($\Delta H = 104$ kcal)

$CH_3-CH_2-H \longrightarrow CH_3\dot{C}H_2 + H^{\cdot}$ (ΔH. 98 kcal)

$CH_3-\underset{H}{CH}-CH_3 \longrightarrow CH_3-\dot{C}H-CH_3 + H^{\cdot}$ (ΔH. 95 kcal)

$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\dot{C}}-CH_3 + \dot{H}$ (ΔH. 92 kcal)

Less energy, More stability.

Stability order: $3^{\circ} > 2^{\circ} > 1^{\circ}$

The more stable the free radical, the more easily it's formed.