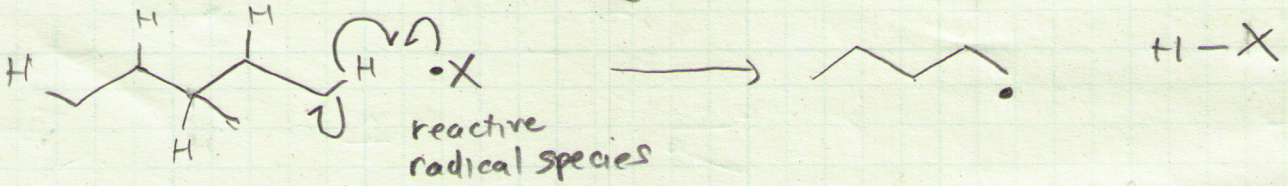
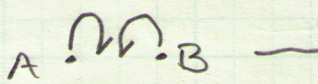
Alkane Radical Chemistry

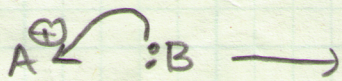


Note: ½ barbed arrow are used to show the movement of a single electron.



½ barbed arrows are used and show where e⁻ is going: between 2 atoms.

Note difference of 2e⁻ movement

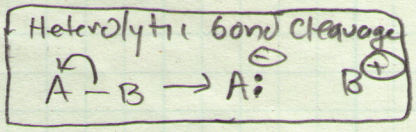


full-head arrow is used and is drawn to show from where e⁻s are coming and the arrow head points which atom is being "attacked"

radical cleavage. 1 of 2 e⁻s in a bond go to each of the flanking atoms

Homolytic bond cleavage

Contrast: Heterolytic bond cleavage



H• •H ⟶ H–H ΔH is (+) or (–) 104 kcal mol⁻¹ ?

H–H ⟶ H• •H " " " " " " ?

Relative bond strength

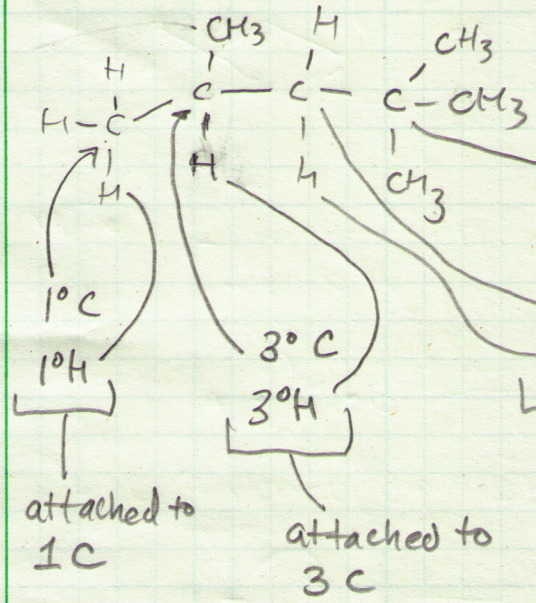
increasing bond length → weakens bond

H–F	H–Cl	H–Br	H–I	
+136	+103	+87	+71	kcal mol⁻¹

why this order?

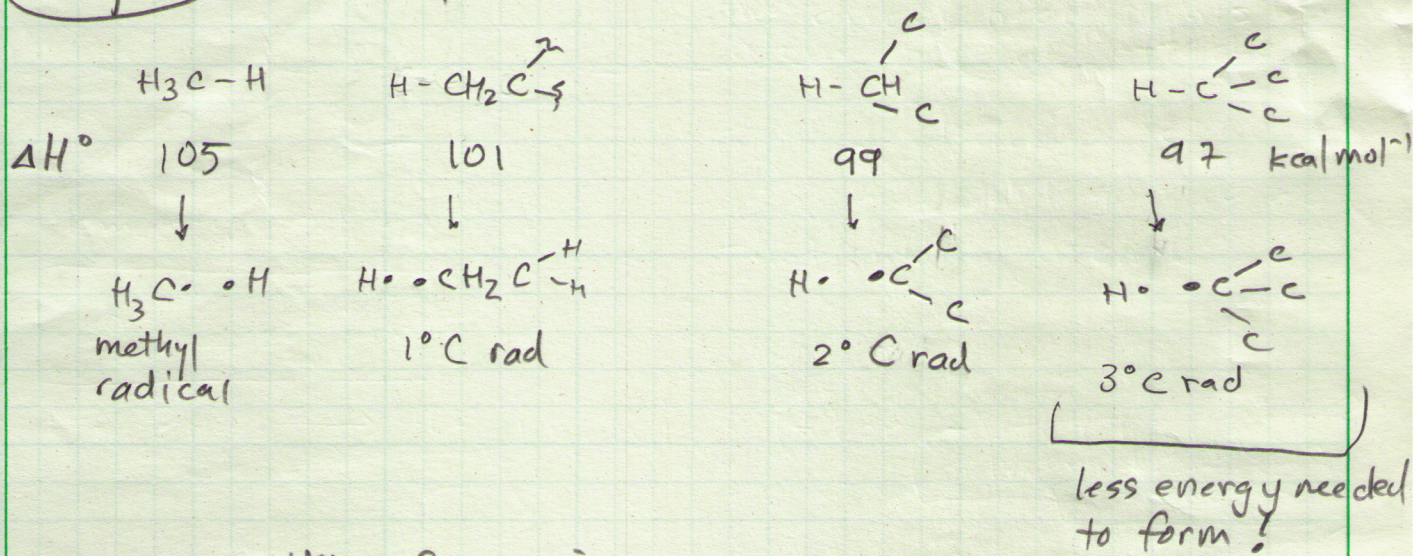
H_3C-F	H_3C-Cl	H_3C-Br	H_3C-I	
+110	+85	+70	+57	kcal mol⁻¹

Let's Look at the strength of the various C-H bonds in an alkane

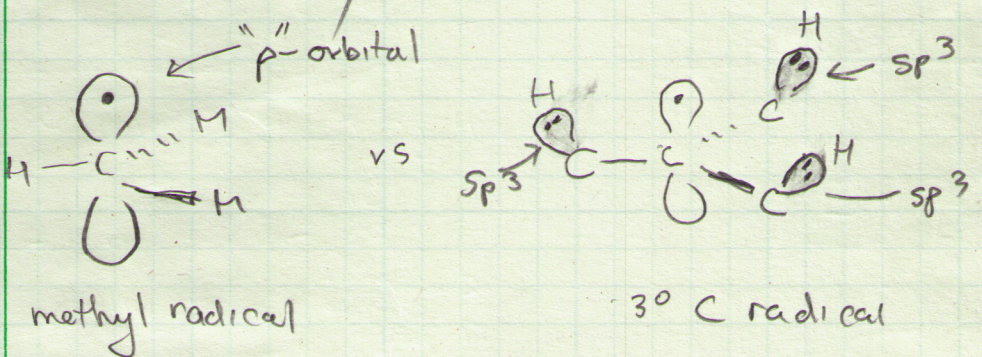


1° - Primary
2° - secondary
3° - tertiary
4° - quaternary

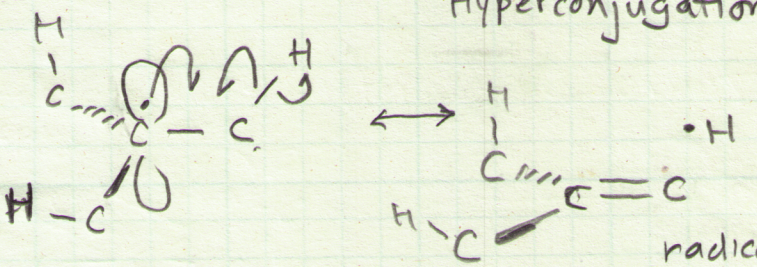
Why?



Look at stability of radicals

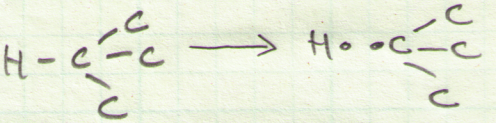


Hyperconjugation (similar to Resonance stabilization) but not exactly

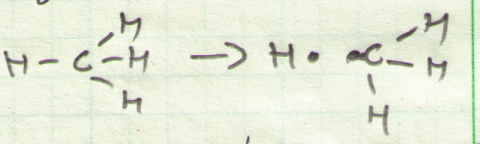


radical is delocalized partially and this gives 3° C radical better stability

making



require less E than



hyperconjugat^{n} not possible.

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chlorination of Methane

$Cl-Cl$	$H-CH_3$	$\longrightarrow$	$Cl-CH_3$	$H-Cl$
+58	+105		−85	−103

$\Delta H^\circ = -25$ kcal mol^{-1} $\quad K_{eq} > 1$ reaction lies to right

Mechanism

Initiation

$Cl-Cl$ —(light ($h\nu$) or Δ (heat))→ $2 \times Cl\bullet$ $\quad +58$ kcal mol^{-1}

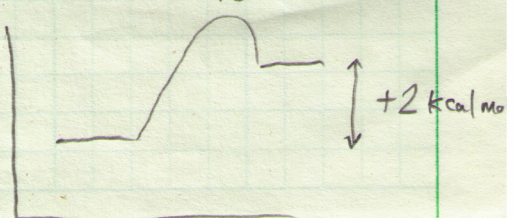
only small amount of this is needed

Propagation

① $Cl\bullet + H-CH_3 \longrightarrow H-Cl + \bullet CH_3$

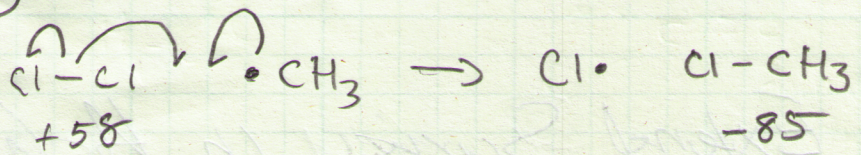
+105 $\quad$ −103 $\quad$ $\Delta H^\circ = +2$ kcal mol^{-1}

TS $Cl \cdots H \cdots C$ (H, H, H) → becoming sp^2 rad (•) will be in p orbital

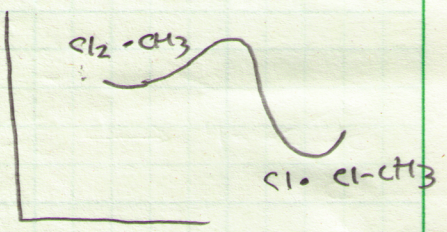


Propagation

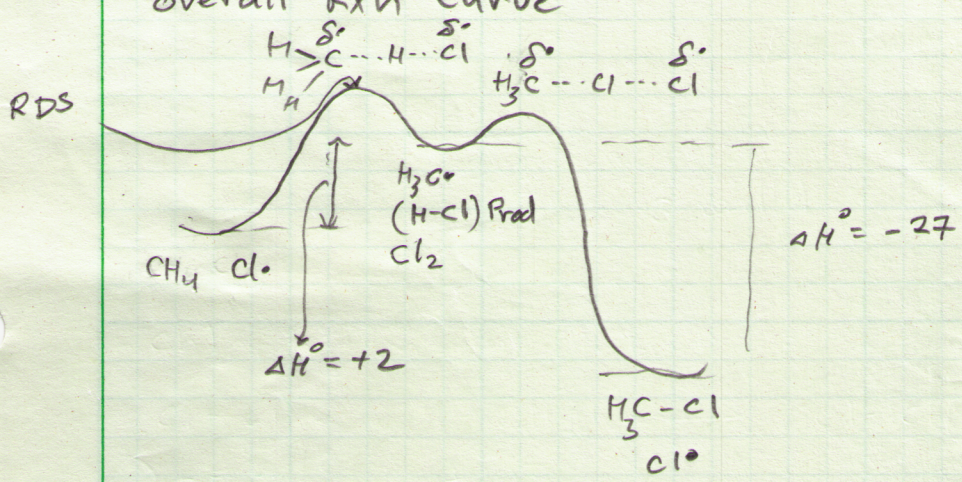
(2)



$\Delta H^\circ = -27 \frac{kcal}{mol^{-1}}$



overall Rxn Curve



Chain Termination Steps (steps that remove radicals from propagat^n)

$Cl\cdot \quad \cdot Cl \longrightarrow Cl-Cl$

$Cl\cdot \quad \cdot CH_3 \longrightarrow Cl-CH_3$

$H_3C\cdot \quad \cdot CH_3 \longrightarrow H_3C-CH_3$