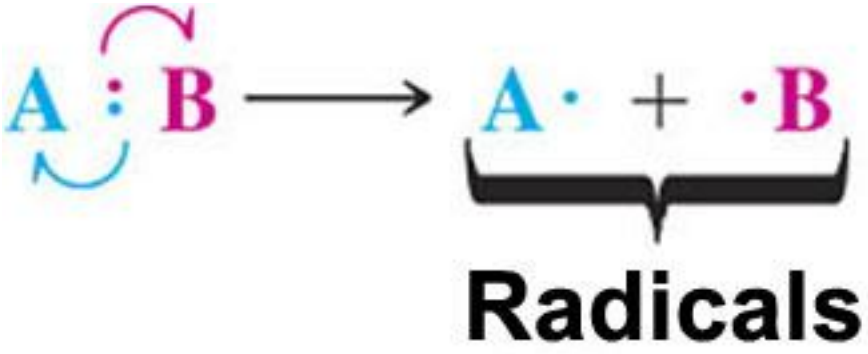
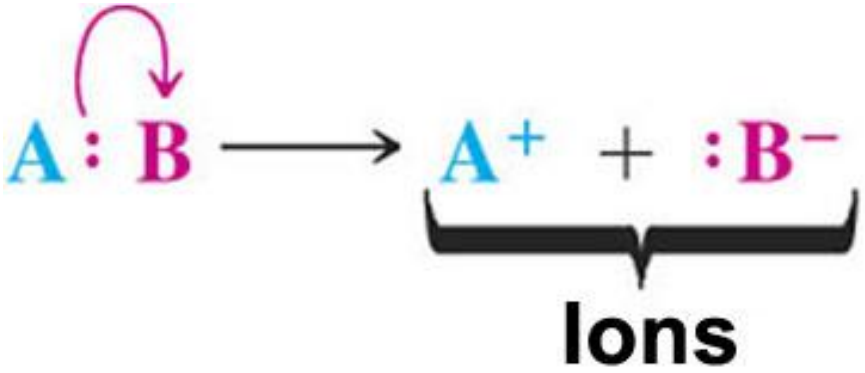
Organic Chemistry Concepts LOKT.09.051

σ-bond reactivity



Bond homolysis

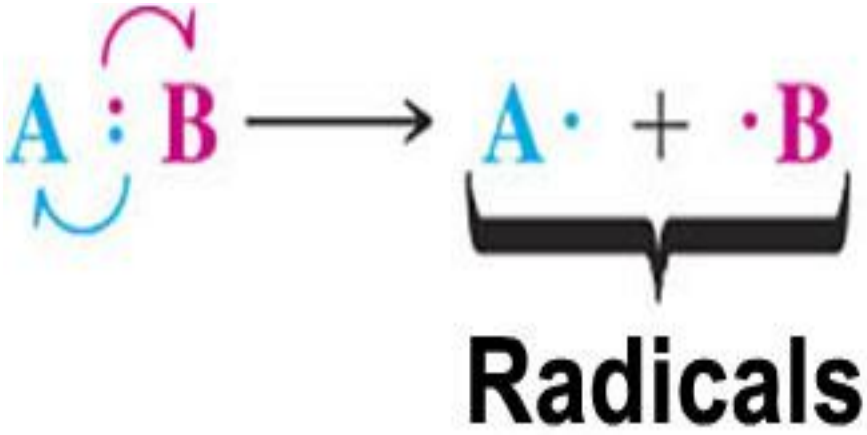


Bond heterolysis

Homolysis: non-polar bond

Heterolysis: polar bond

Radical mechanism



Bond homolysis

Bond energy (kJ/mol)

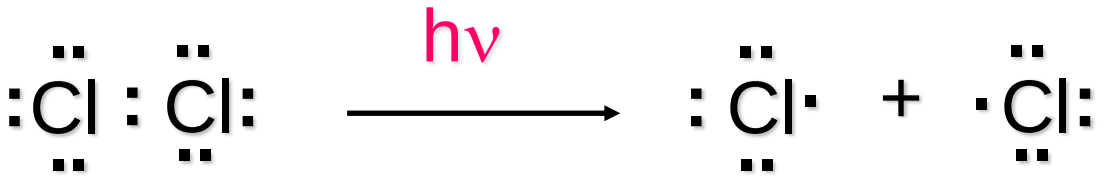
H-H	436	H-C	413
C-C	348	H-N	391
N-N	170	H-O	366
O-O	145	H-F	568
F-F	158	H-Cl	432
Cl-Cl	243	H-Br	366
Br-Br	193	H-I	298
I-I	151		

From where energy comes?

- **Thermolysis**
- **Photolysis**
- **Chemically induced homolysis**

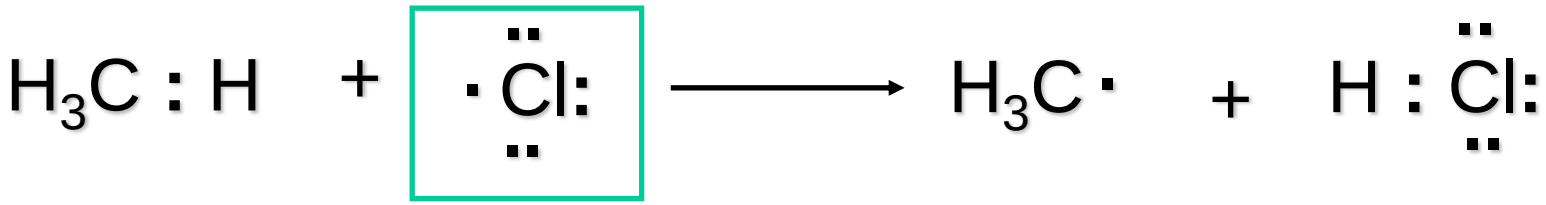
$$CH_4 + F\text{-}F \rightarrow CH_3^{\bullet} + H\text{-}F + F^{\bullet}$$

Photochemical initiation

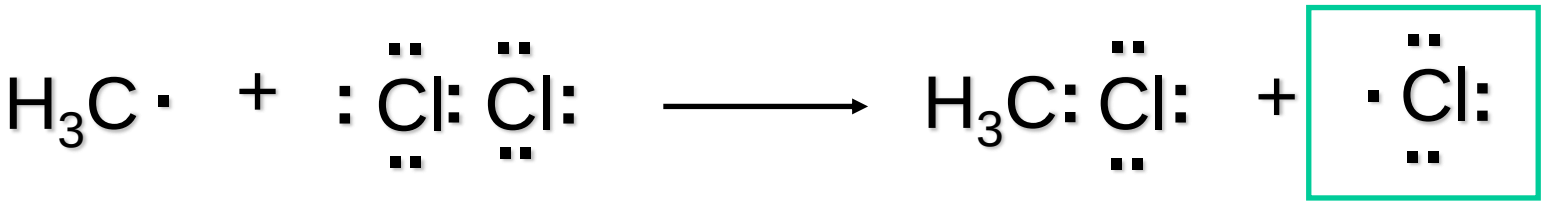


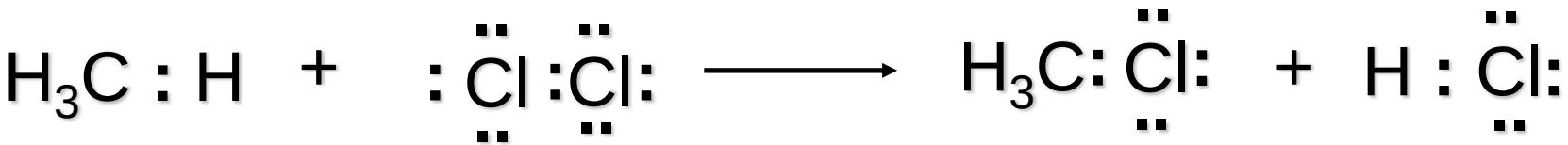
Radical substitution reaction mechanism

First step:



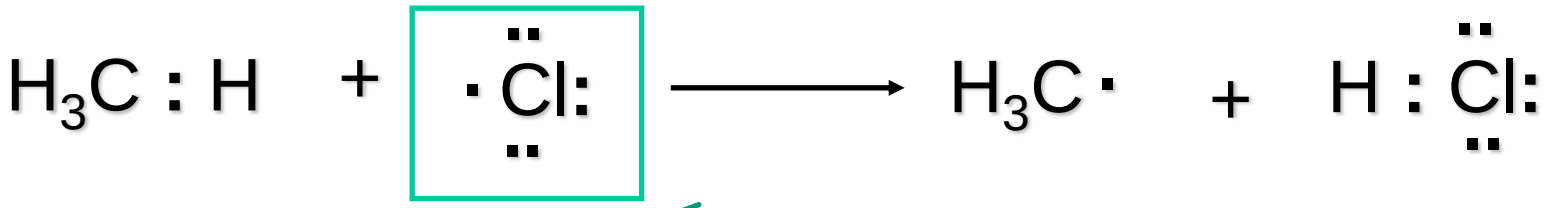
Second step:



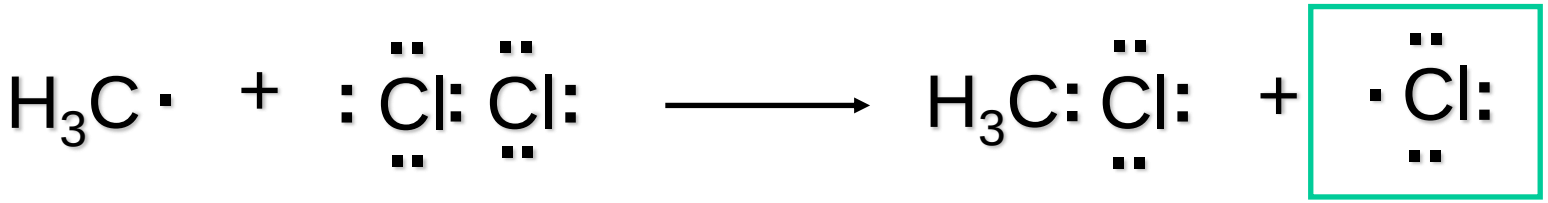


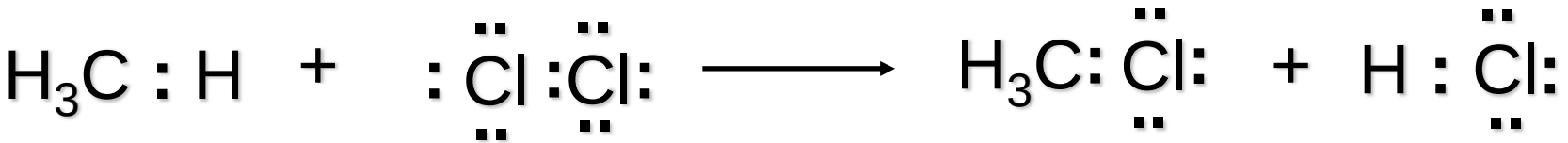
Radical substitution reaction

First step:

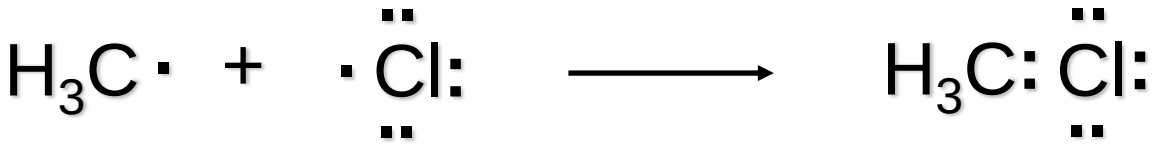


Second step:



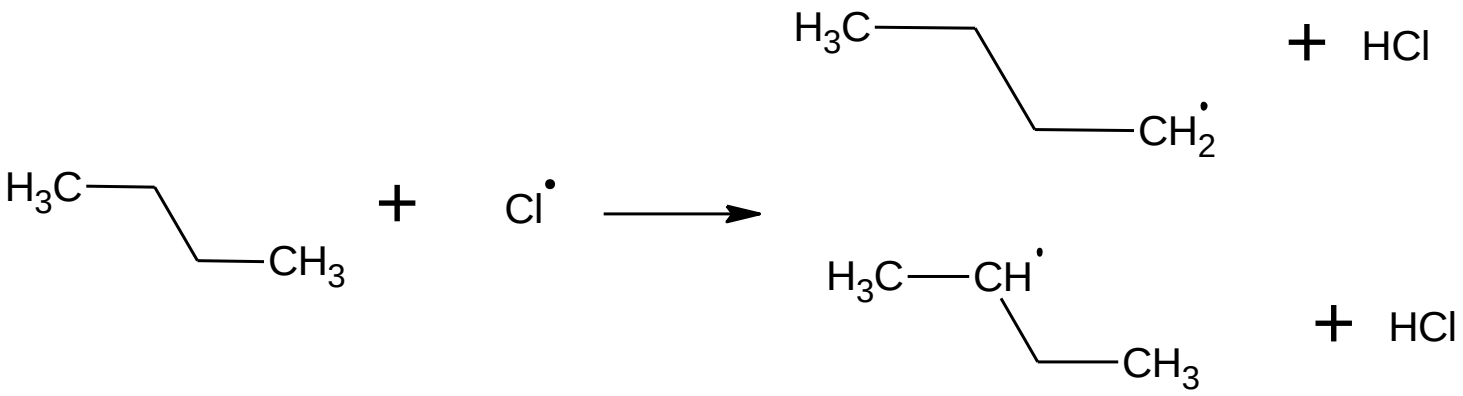


Termination



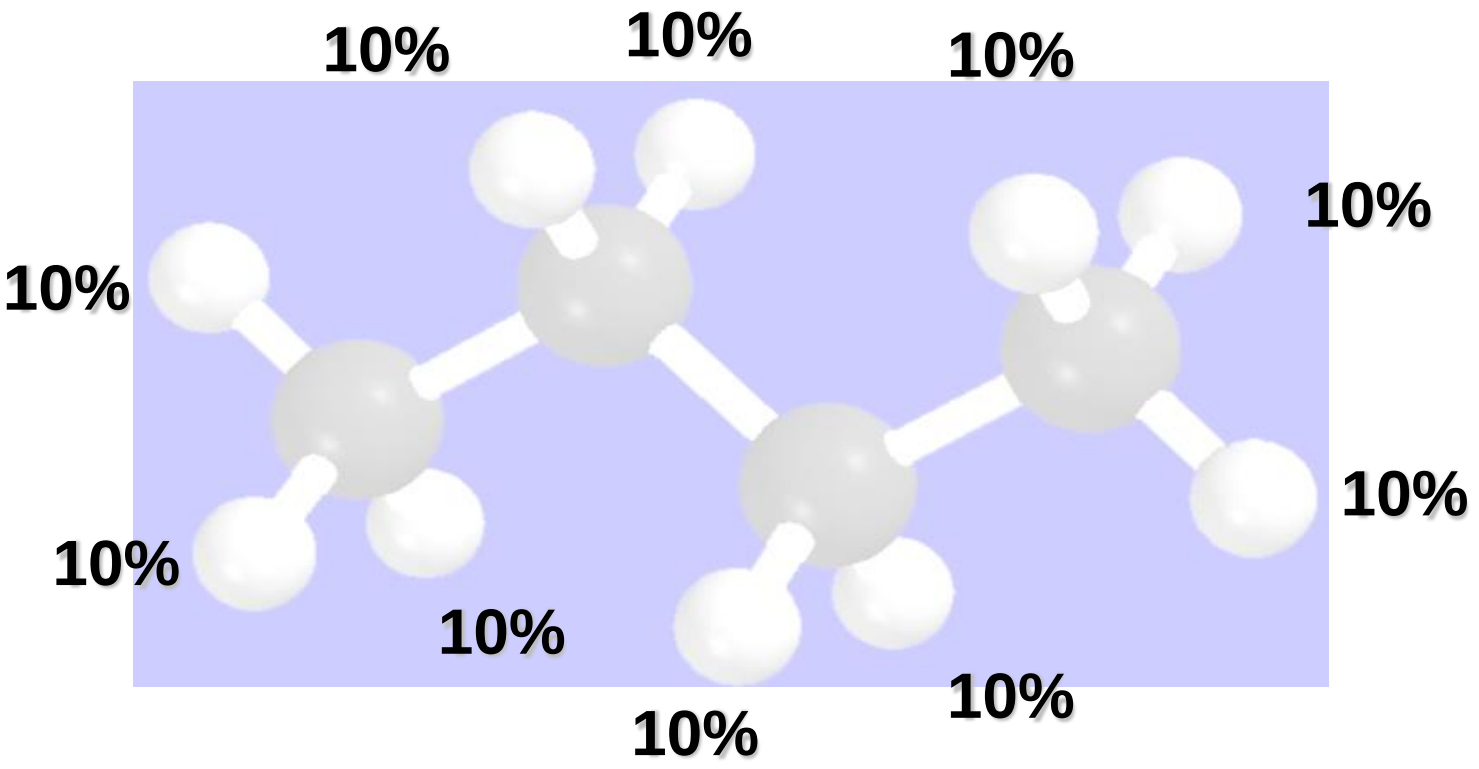
Very small amount of product via this step.

Butane chlorination



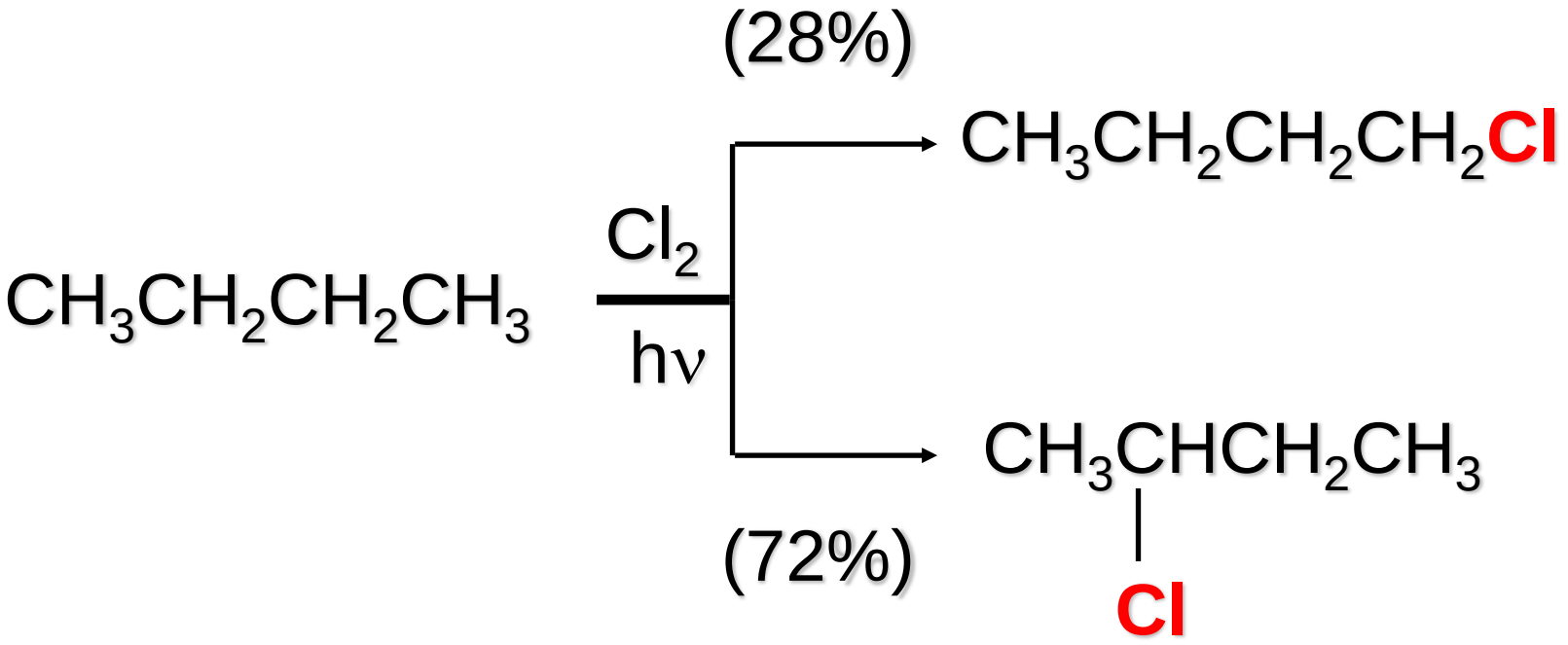
Frequency of hydrogen atom occurrence

C_4H_{10}

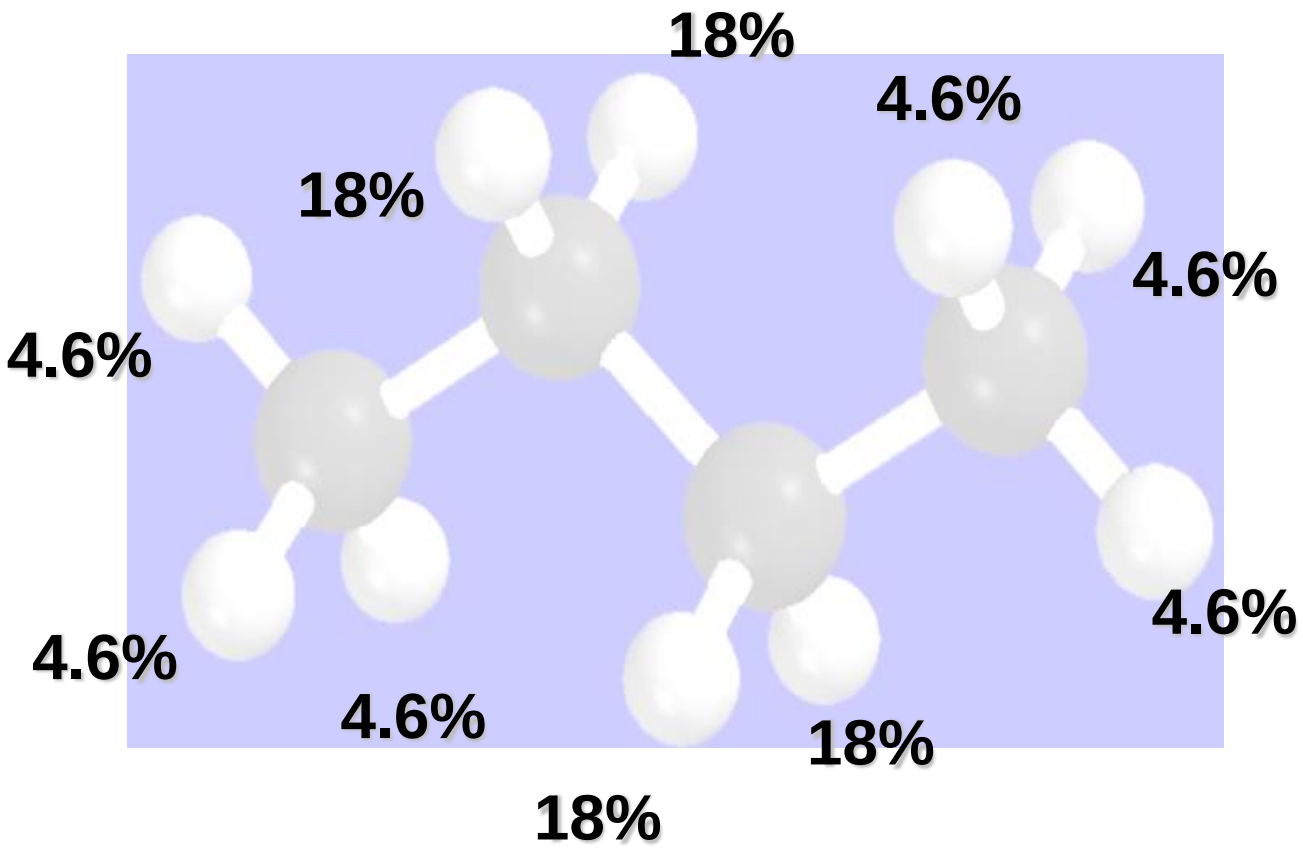


Buthane clorination

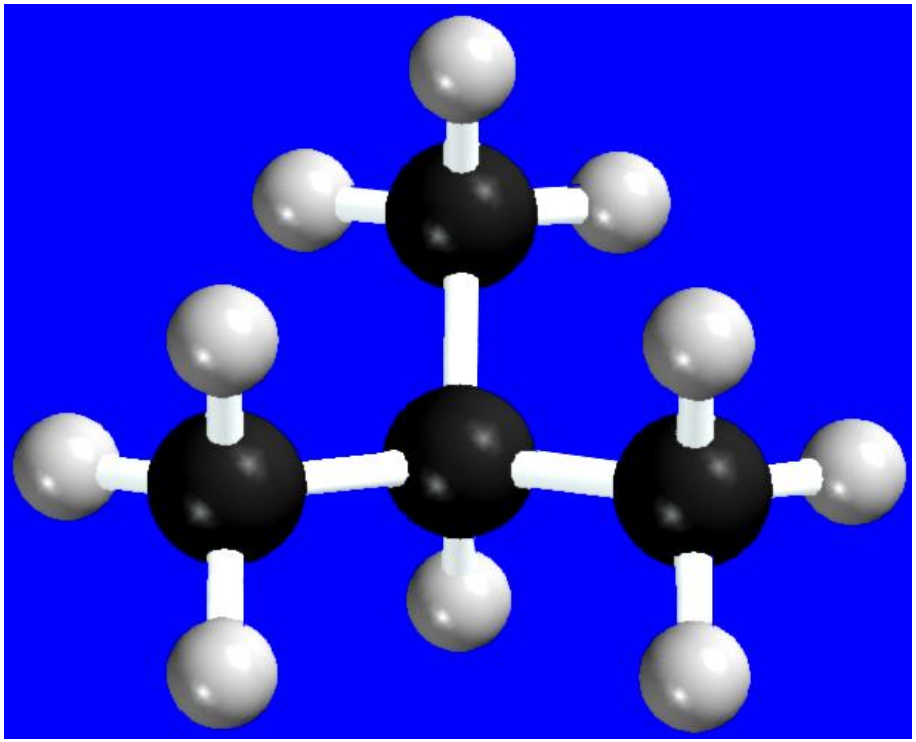
1-chlorobutane and 2-clorobutane



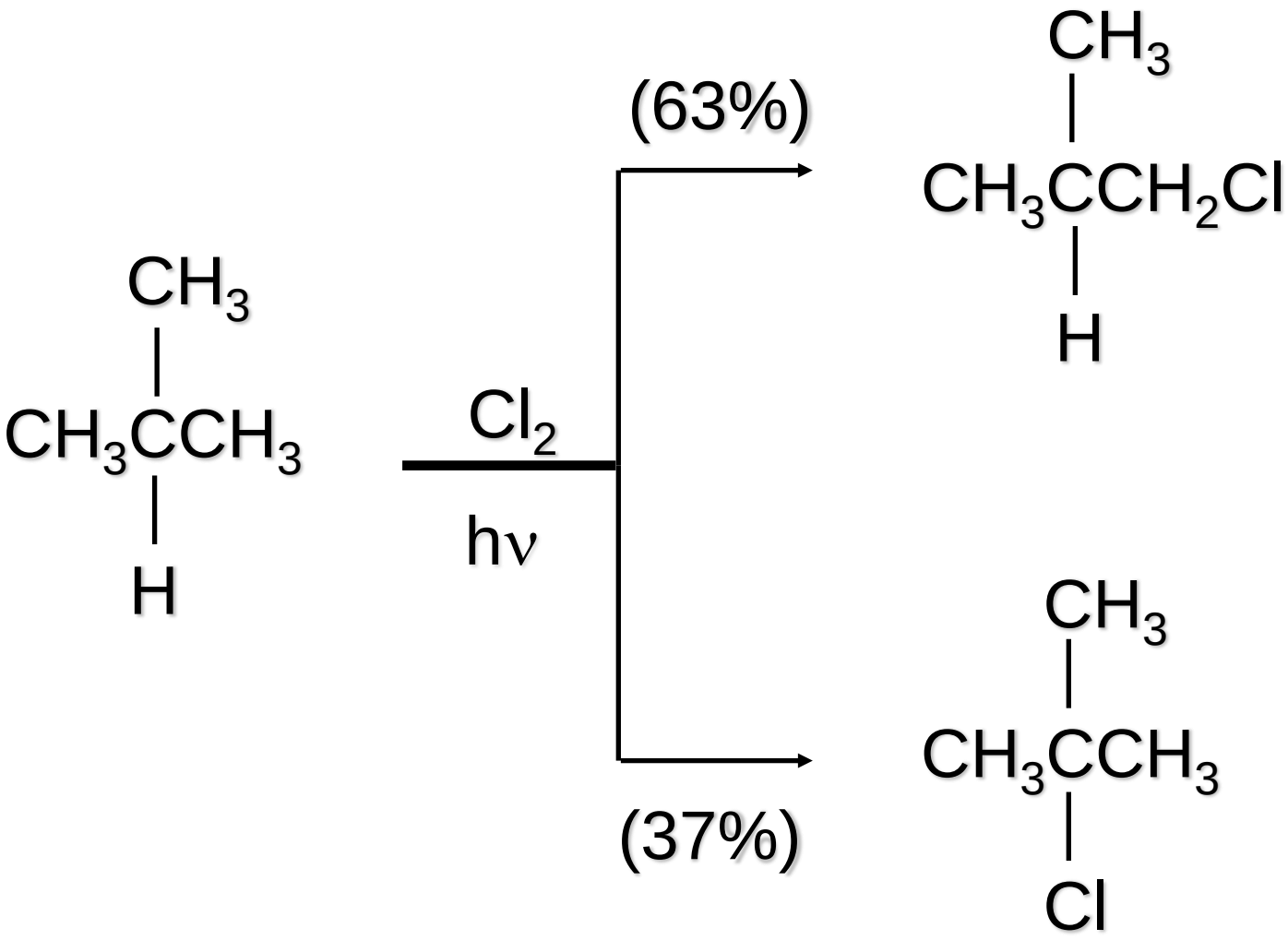
Reactivity is different



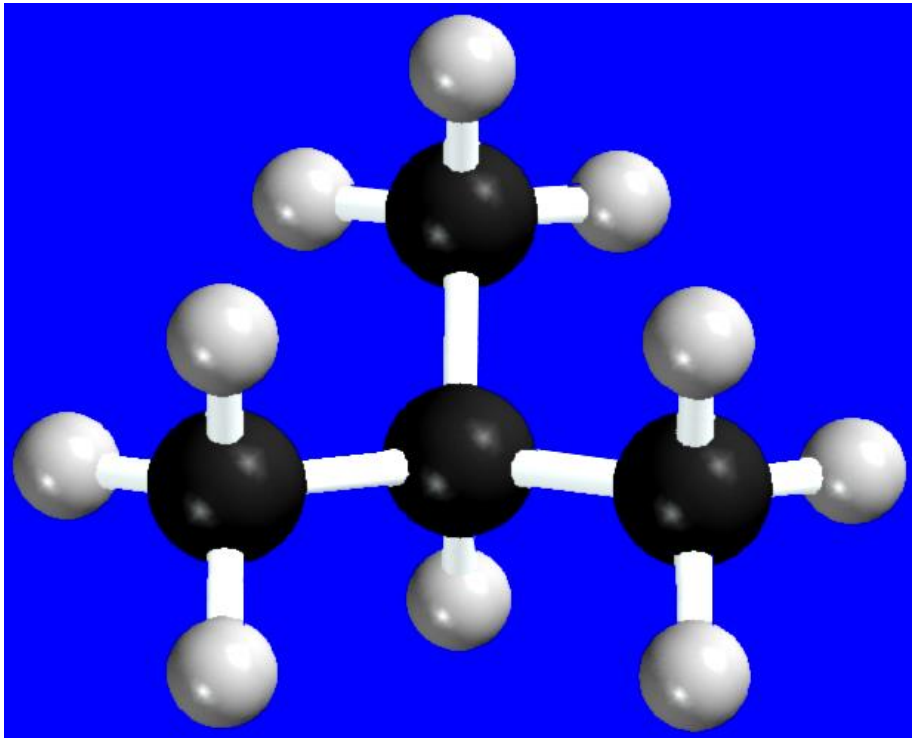
10 hydrogen atoms at CH_3 groups and 1 at tert C atom



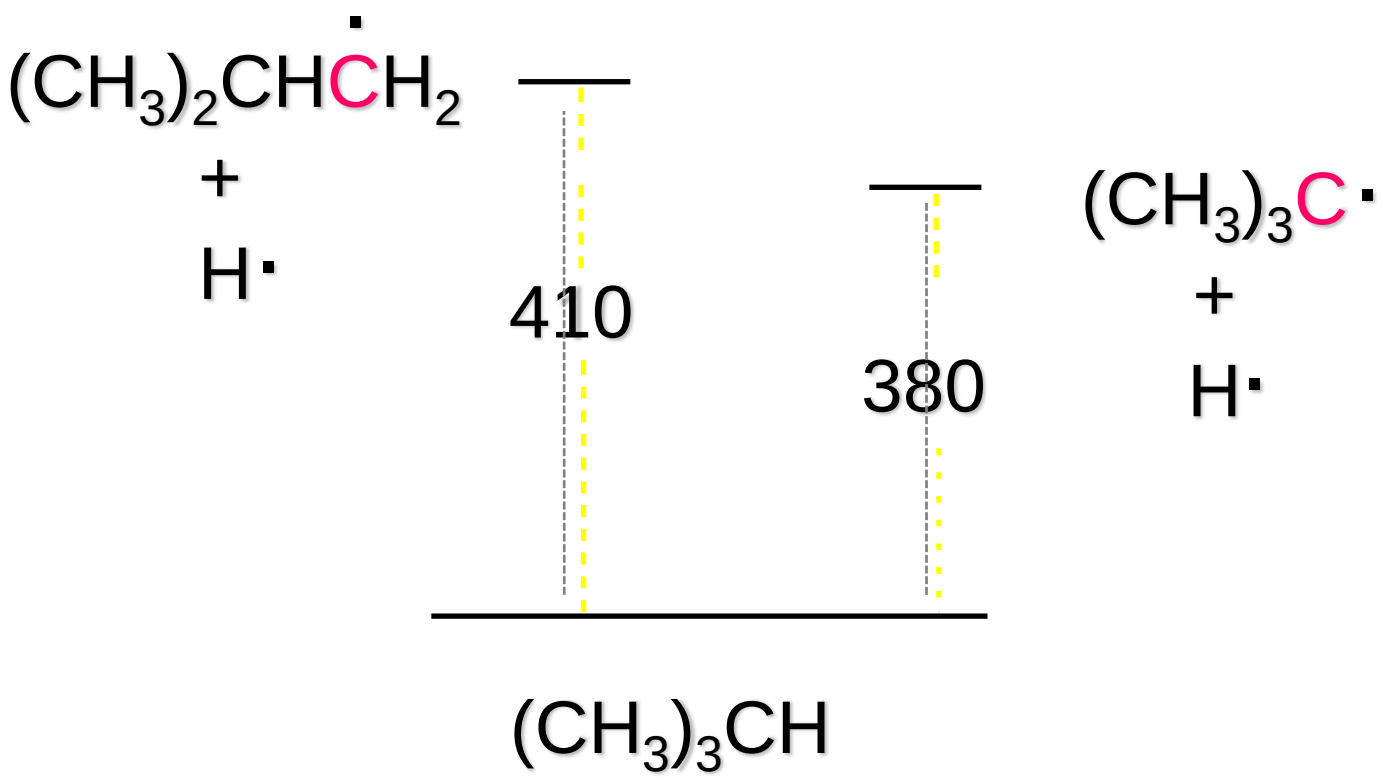
Methylpropane chlorination yields

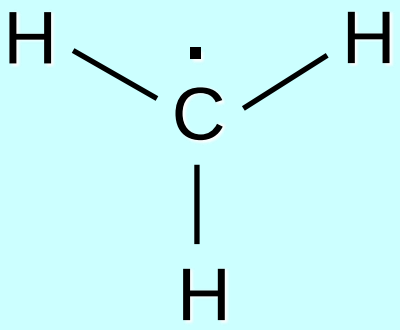


7.0%



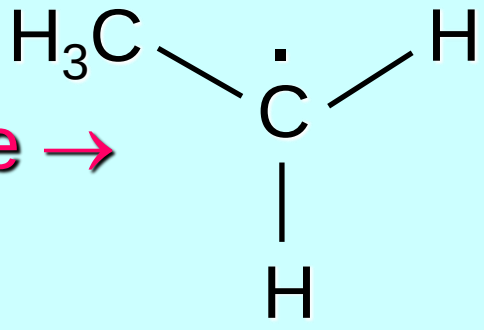
37%


(CH3)2CHCH2
+
H·
410
380
(CH3)3C·
+
H·
(CH3)3CH



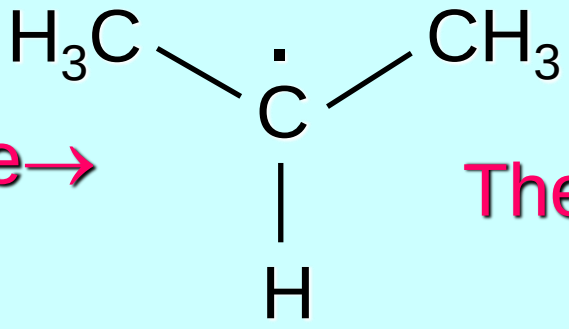
methyl

Stable →



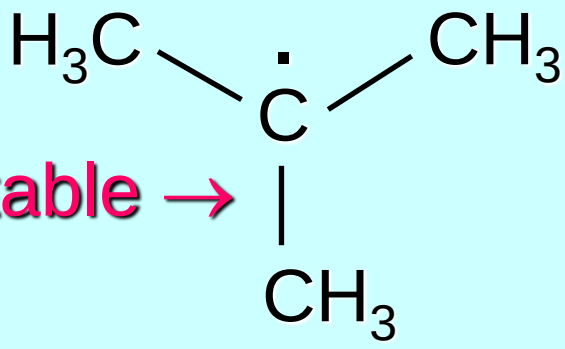
ethyl

More stable→

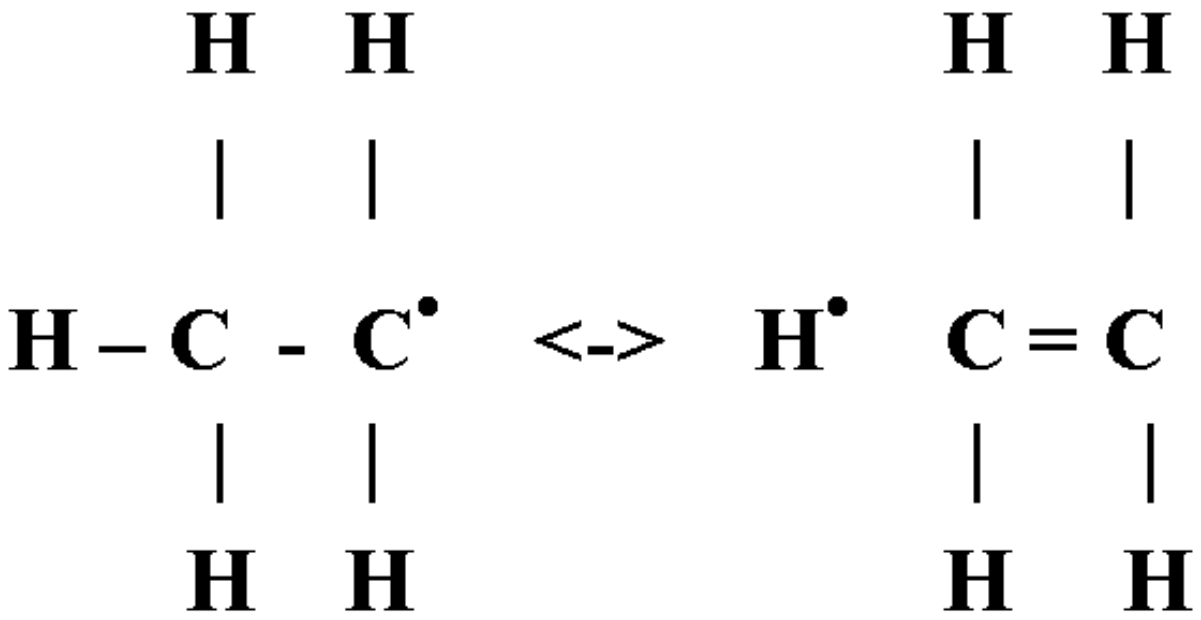


iso-propyl
(sec)

The most stable →



tert-butyl
(*tert*)

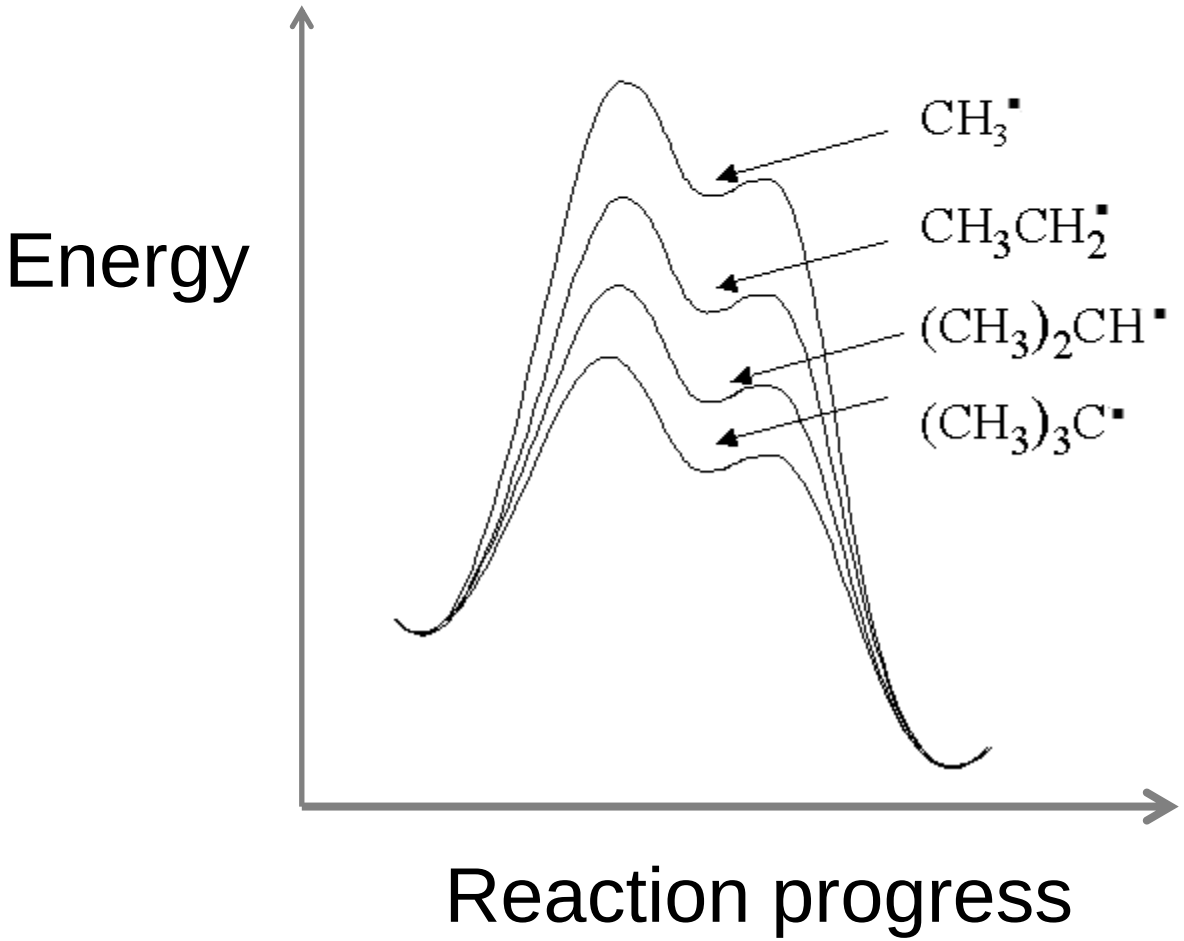


Hyperconjugation

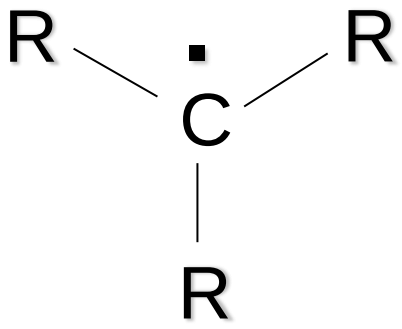
C-H bond dissociation energies kJ/mol

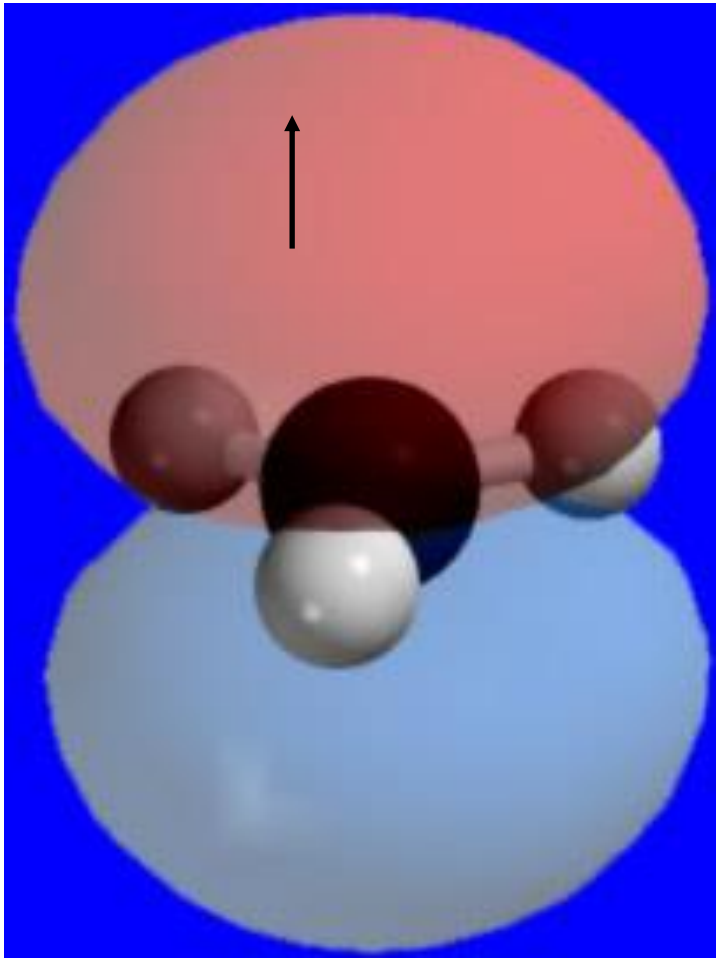
- Me-H **439**
- $MeCH_2$-H **423**
- Me_2CH-H **412**
- Me_3C-H **404**
- CH_2=$CHCH_2$-H **362**
- $PhCH_2$-H **370**
- Ph_2CH-H **341**
- Ph_3C-H **298**
- CH_2=CH-H **465**
- CH ≡ C-H **556**

Radical stability



Radical structure





Combustion

$CH_3\text{-}CH_2\text{-}CH_3 + 5\ O_2 \longrightarrow$

$\longrightarrow 3\ CO_2 + 4\ H_2O + \text{heat}$

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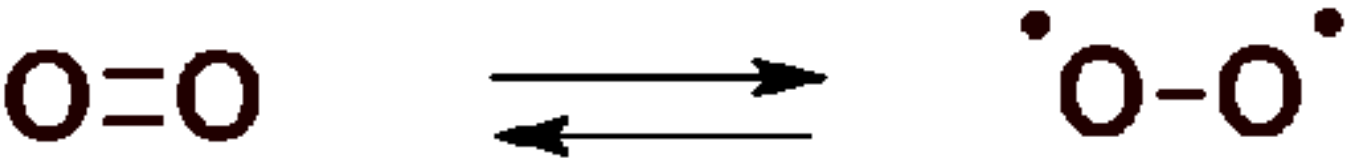

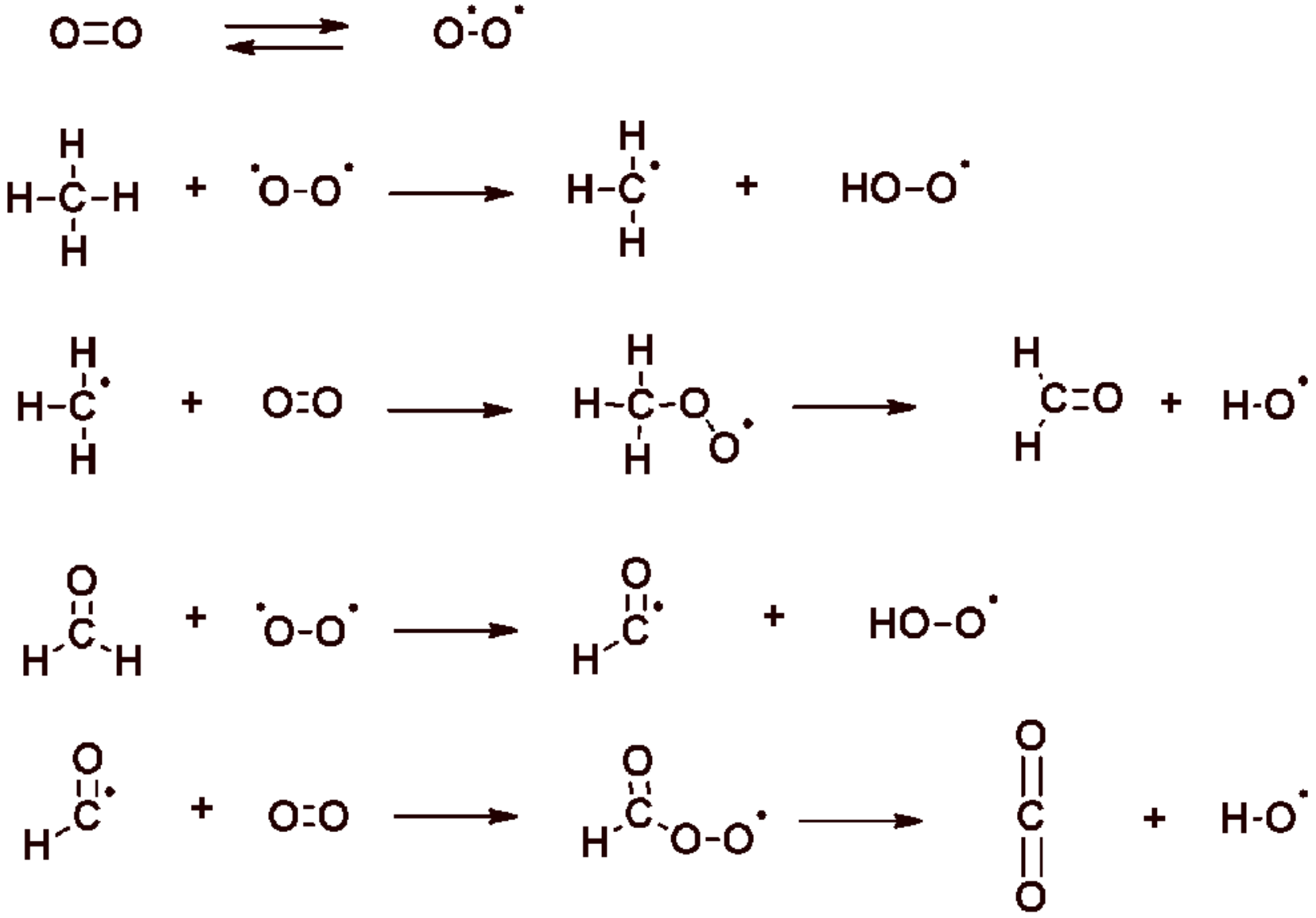

Redistribution of electrons stabilizes molecules