# **RECALL:**

# Halogenation of alkanes:

- requires light or heat to cause a reaction between the starting material and halogen.

# Example:



- requires light or heat to cause a reaction between the starting material and halogen.



 $C_7H_{14}$ 

Initiation Step:



Propagation Step 1



Propagation Step 2



Termination Step: Radicals Recombine -Very minor component of the reaction



Two alkyl radicals combining is highly unlikely because the chances of them finding one another is very low (they are low in concentration) – above also very crowded (steric effect)

$$Br \cdot + Br \longrightarrow Br_2$$

## **Stability of radicals:**

- Stability increases with alkyl substitution
- Alkyl groups are polarizable and donate electrons to electron deficient sites better than hydrogens (this is called **inductive effect** and occurs through sigma bonds)



1,1,4-trimethylcyclohexane



CI

Neopentane (2,2-dimethylpropane)



2, 5-dimethylhexane

# **Reactivity and Selectivity (Hammond Postulate)**



I<sub>2</sub> does not react as above

# NOTE:

More reactive reagents give less selective products Less reactive reagents give more selective products

## **For Exothermic Reactions**

-The transition state resembles the starting material

### **For Endothermic Reactions**

-The transition state resembles the products

## **Energy Diagrams for Halogenation Reactions**

Bromination  $(\Delta H > 0)$ TS *Fluorination* ( $\Delta H < 0$ ) Exothermic Endothermic Pdt S.M small small (TS similar to Е SM) Е large large Pdt S.M Rxn coordinate Rxn coordinate E = energy

E = energyTS = transition state SM = starting material

#### **Reactivity TREND:**

 $F_2 > Cl_2 > Br_2 >> I_2$  Iodine does not react



 $\Delta H = -35$  kcal/mole Exothermic

$$Br \cdot + - \stackrel{|}{C} - H \longrightarrow Br - H + - \stackrel{|}{C} \cdot$$

 $\Delta H = +16$  kcal/mole Endothermic

## Selectivity TREND:

Br• > CI•	> F•
most selective	least selective

endothermic exothermic

Bromine atom "searches" the molecule to create the most stable radical Fluorine atom is small and feels the loss of an electron much more than bromine

- Fluorine is less precise and reacts immediately

#### Naming of Alkyl Halides = Haloalkanes

CH <sub>3</sub> Cl	$CH_2Cl_2$	CHCl <sub>3</sub>	CCl <sub>4</sub>
Methyl chloride	Methylene chloride	Chloroform	Carbon tetrachloride
Chloromethane	Dichloromethane	Trichloromethane	Tetrachloromethane

#### **Structure and Nomenclature**

- 1) Find longest chain with largest number of branches
- 2) Number from end so as to give 1<sup>st</sup> halogen the lowest number
- 3) Name prefix with "halo" (chloro, bromo, iodo, fluoro) OR name alkyl and add halide (chloride, bromide, iodide, fluoride) as the suffix

#### **Examples:**







Isopropyl Bromide 2-Bromopropane

tert-Butyl fluoride 2-Fluoro-2-methylpropane

Neopentyl chloride 1-Chloro-2,2-dimethylpropane



2 -chloro -4-methylhexane



Fluorocyclopropane

Cyclopropyl fluoride



5-Butyl-4-iodotetradecane

# **Applications of Haloalkanes**

1.) Halothane (anesthetic)



- 1,1,1-trifluoro-2-bromo-2-chloroethane
- 2.) Freon = refrigerants/coolants



3.) 1,1-dibromo-2-chloroethane = male contraceptive (sperm count drops down to zero from 100 million/mL)



# **Physical Properties of Alkyl Halides:**

- Governed primarily by dipole-dipole interactions, more polar than hydrocarbons/alkanes.
- High MP and BP relative to hydrocarbons of similar molecular weight
- Good solvents for organic compounds e.g. methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) and chloroform (CHCl<sub>3</sub>) are very common.
- If % composition  $\ge 65\%$  halogen by weight, then more dense than water ( $\rho > 1.0$  g/cm<sup>3</sup>)
- Immiscible (insoluble) in H<sub>2</sub>O, which floats on top of the halide

# **NEXT SECTION: Lecture Outline 3: Stereochemistry and Chirality**

# Introduction to Stereochemistry and Chirality (terminologies)

*Chiral* object or molecule: has a non-superimposable mirror image *Achiral* object: not chiral, has a superimposable mirror image

Tetrahedral carbon with 4 <u>different</u> groups are said to be **CHIRAL** and are said to contain a **STEREOGENIC** (CHIRAL) CENTER



1850 - Louis Pasteur separated the "right-handed" and "left-handed" forms of tartaric acid crystals (from wine)

 $\underline{1876}$  - J. van't Hoff and Le Bel proposed that differences are due to tetrahedral geometry of carbon

- Kolbe did not receive van't Hoff's idea very well

<u>1901</u> - J. van't Hoff was the first recipient of the Nobel Prize in Chemistry