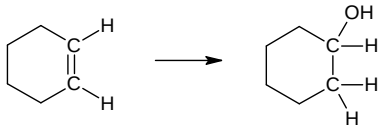
1. A Chemical Puzzle
2. The Polyalkene Industry & You

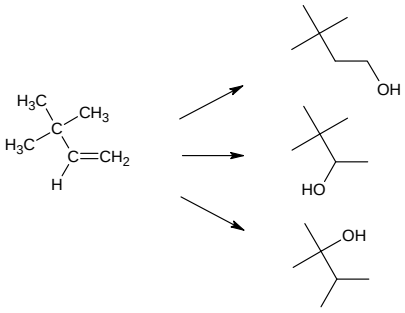
Ch 5.6-5.8

Organic Chemistry: Inquiry or Industry?



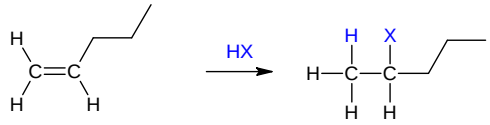
- Since all 3 reagents work
  - H_2O, cat. H_2SO_4
  - $Hg(OAc)_2$, H_2O, then $NaBH_4$, OH^-
  - B_2H_6 then H_2O_2, NaOH
- Inquiry & industry are disconnected?

- Since only one reagent works in each rxn, industry requires inquiry?

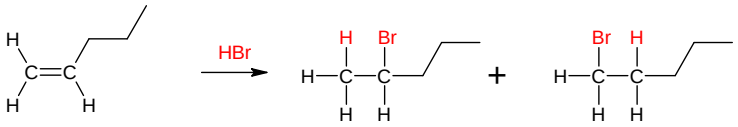


An "anti" Markovnikov controversy

- Markovnikov



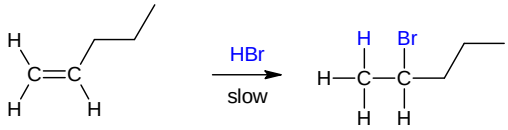
- Other scientists



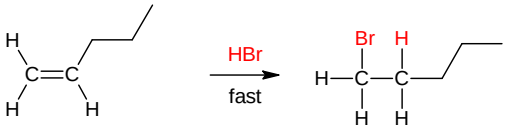
  - Different procedures, different materials?
  - "Butterfly" effect? (different initial conditions)
  - HBr "exceptionalism?
  - Markovnikov wrong?
  - "Carbocation stability" hypothesis wrong?

Solution: Peroxide (etc.) impurities

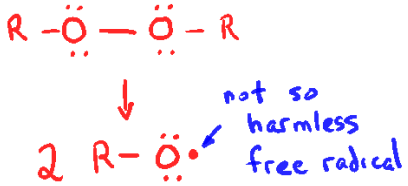
- Dark, cold, peroxide-free



- Illuminated, warm, peroxides added



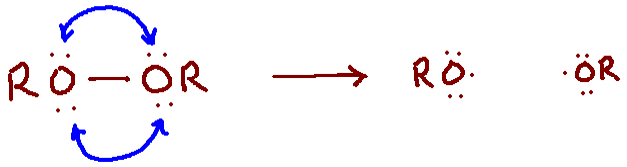
  - "peroxide" effect leads to
    - different mechanism w/ different regioselectivity
    - faster reaction (no longer see Markovnikov result)



Strong & Weak Covalent Bonds

- Some strong bonds (typical BDE)
  - H-C (410)
  - H-O (440)
  - H-F (570)
  - C-C (380)
  - C-O (380)
  - C-F (480)
- Pi effect
  - C=C (243 pi)
- Larger atom effect
  - H-S (380)
  - H-Cl (430) C-Cl (350)
  - H-Br (370) C-Br (300)
  - H-I (300) C-I (240)
- Lone pair effect
  - F-F (154), Cl-Cl (240), Br-Br (190), I-I (150)
  - RO-OR (160)

How Do Lone Pairs Weaken Bonds?



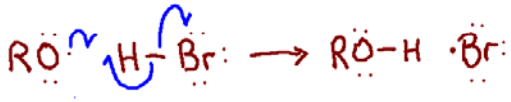
- Pauli repulsion between lone pairs disappears when bond breaks
  - Varies w/ dihedral angle
  - Rotation barriers
    - CH_3CH_3 12 kJ/mol
    - HOOH 40? 50? *(stay tuned)*

Mechanistic features of reaction

- Complicated
  - 3 phenomena explained:
    - peroxide effect, HBr exceptionalism, regioselectivity
- Peroxide role
  - Accelerates reaction, but is consumed → initiator
  - Introduces free radicals (RO)
  - Which breed more radicals (Br)
- Multi-step chain reaction
  - One radical always makes another
    - But [radical] always small
  - C=C + HBr → HC-CBr
- Termination
  - Mutual annihilation of radicals when they meet
  - A little "inhibition" goes a long ways

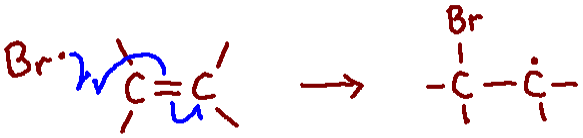
Initiation Steps

- OO BDE = 160
  - very endothermic → slow (sometimes light-assisted)
  - "weakest link" → peroxide effect
- [RO] = tiny

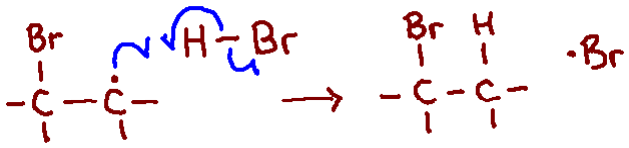


- **Hydrogen atom abstraction** exothermic HBr (368) → HO (440)
- Other possibilities: exo HCl (431), HI (297) endo HF (570)

Propagation Steps (Chain Mechanism)



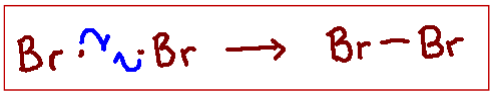
- **Bromine atom addition** exothermic CC pi (243) → CBr (300)
- Other possibilities: exo Cl addn (350), endo I addn (238)

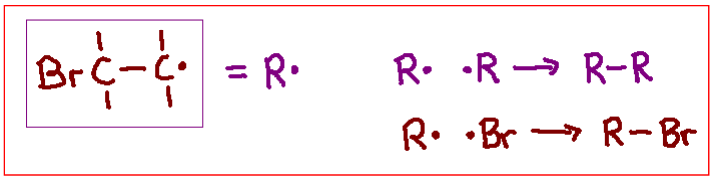


- **Hydrogen atom abstraction** exothermic HBr (368) → HC (410)
- Other possibilities: endo HCl (431) → HC (410)

Termination steps (when radicals meet)

- Each combination annihilates two radicals (two chains)
  - Best results if [radical] very small
  - Typical chain maybe 10,000 "turnovers"



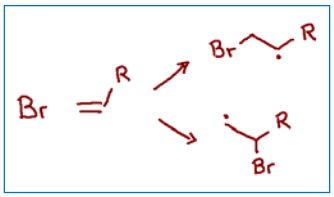


Taking stock

- (Cold, dark) Peroxide effect
  - OO bond is weakest
  - But heat (or light) still needed to create RO
- HBr exceptionalism
  - HF bond too strong for abstraction by anything
  - HCl bond too strong for abstraction by C•
  - Cl bond too weak for addition to C=C
  - HBr is "just right" (every step exothermic)

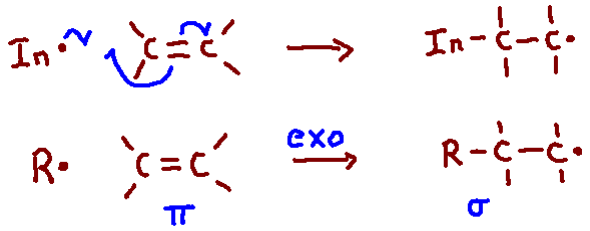
Regioselectivity Explained

- Stability of C free radicals: 3° > 2° > 1°
  - Like carbocation stability order
  - H → R swap is stabilizing
- Hyperconjugation less effective in radicals
  - H → R = 70 in C+
  - H → R = 12 in C•
  - H → R = 7 in alkene
- Conjugation is still more effective
  - H-CH_2R (423)
  - H-CH_2CH=CH_2 (372)
  - H-CH_2Ph (378)

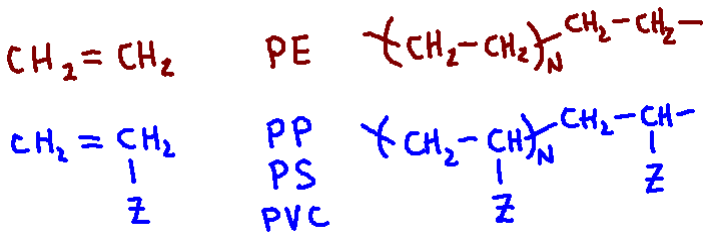


Free Radical Polymerization of Alkenes

- Variety of mechanisms
  - Free radical chain is just one possibility
  - Different polymers from different reagents/mechanisms



Alkene Polymers are Not Alkenes



- PE = polyethylene (low density LDPE, hi density HDPE)
- PP = polypropylene (Z = CH_3)
- PS = polystyrene (Z = Ph)
- PVC = polyvinyl chloride (Z = Cl)

Plastics are largely polyalkenes

MAJOR END USE MARKETS

END USE	US MARKET 2000 (kTons)	Percent of Total Market
PACKAGING (Bottles, Film, Cups, etc.)	9683	25%
BUILDING & CONSTRUCTION (Pipe, Siding, insulation, etc.)	8554	22%
CONSUMER & INSTITUTIONAL (Toys, Housewares, Medical, etc.)	5290	13%
TRANSPORTATION	1846	5%
FURNITURE & FURNISHINGS	1694	4%
ELECTRICAL/ELECTRONICS (W&C, Computers, Appliances, etc.)	1461	4%

only 11% was exported

U.S. Manufacture of Alkene Polymers

- August '09 (American Chemistry Council)
  - All PE – 3.3×10^9 lbs
  - PP – 1.4×10^9 lbs
  - PS – 0.4×10^9 lbs
  - PVC – 1.2×10^9 lbs
  - Total – 6.3×10^9 lbs
  - **>20 lbs/American in one month of a bad economy**
  - Much higher than rest of world
  - Plastics have lone lifetimes. # Uses? Disposal?