*CHEM 242 – Lecture 2 08/01/2014*

Overheads: - Outline

- Feedback & Questions

Go over feedback/questions (overhead)

Recap Monday

Radical: atom with unpaired electron *e.g.* CH3•



Radical Halogenation:



Mechanism: three “parts”



Then… radical reacts with alkane:







🢡 Called a Radical Chain Reaction: Br• kicks off chain reaction = propogation

Always has 3 parts:

* Initiation: make small amount of radicals
* Propagation: form products 1000’s of times
* Termination: radicals eventually get used up

🢡 Reaction works for Br2 and Cl2 *only*



What if Molecule has different H’s?



Why? 2° radical > 1° radical

🢡 like C+, R3C• is electron deficient more sub = more stable

🢡 ratio of products results from combination of probability (# of H’s)

and radical stability

Throw in a Wrench:



Why? Compare thermodynamics of propagation steps

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Br2 |  | Cl2 |  |
| Step 2a | +55 kJ/mol | endo | -10 kJ/mol | exo |
| Step 2b | -90 kJ/mol | exo | -90 kJ/mol | exo |
|  | -35 kJ/mol |  | -100 kJ/mol |  |



Hammond Postulate: T.S. is more like the species to which it is closer in energy

Br2: endothermic RDS Cl2: exothermic RDS

TS more like intermediate (radical) TS more like reactants

aka “late TS” aka “early TS”



stability of radical makes more difference to Br2 reaction (TS more like radical)

Br2 more selective