*CHEM 242 – Lecture 3 10/01/2014*

Overheads: - Outline

Test dates: Midterm moved to Feb 10

Recap Chain Reactions: 3 parts to mechanism?



Selectivity: more substituted radicals formed more easily

BUT, Cl2 less selective than Br2

Br2: endothermic RDS Cl2: exothermic RDS

TS more like intermediate (radical) TS more like reactants

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

Br2 more selective

Why is Br\* RDS endothermic, but Cl\* exo?

- only difference is energy of reactants!

🢡 Cl\* must be higher E (less stable) than Br\*

H°f = +122 kJ.mol H°f = +96 kJ.mol

Cl\* higher E wants to react more

Clarify: talking about stability of Cl• vs Br• (= reactant, not product)



SO, Cl• higher E, more reactive, 🢡 reacts faster, grabs whatever it can

Br• reacts slower, more choosy (selective) 🢡 waits for 3° > 2° > 1°

I• even more stable 🢡 too choosy! Doesn’t react at all

F• too reactive 🢡 reacts with anything it can find!

How much less selective is Cl• ?

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | 3° > | 2° > | 1° |  |
| Br• | 1600 | 82 | 1 | } Can use to predict ratios |
| Cl• | 5 | 3.8 | 1 |

Amount 3° = (#3°H)(3° preference) = x % 3° = x / (x+y+z) x 100%

2° = (#2°H)(2° preference) = y % 2° = y / (total) x 100%

1° = (#1°H)(1° preference) = z % 1° = z / (total) x 100%

Total = x+y+z



3° = (0)(5) = 0

2° = (2)(3.8) = 7.6 % 2° = 7.6 / (13.6) x 100% = 56%

1° = (6)(1) = 6 % 1° = 6 / (13.6) x 100% = 44%

Total = 13.6

Same as experimental!

*NOTE:* Unlike carbocations, radicals do not rearrange, so ratio “stays” as predicted

“Homework”

1) Predict Br2 ratios (should be 4:96!)



2) Predict ratios for:

Resonance-Stabilized Radicals:

🢡 get 2 products (ratio depends on conditions)



🢡 BUT… there is a problem! Br2 can react directly with C=C! (CHEM 241)



Solution: use another source of Br•

NBS = N-bromosuccinimide

🢡 NBS does same reaction as Br2, but avoids competing Electrophilic Addition