skip 11.3, 11.5.2.1 p326-327 except NBS, 11.5.2.2 p330-331, 11.5.2.3, 11.6

Free Radical Reactions

1. general properties of radicals
   1. unpaired electron, slightly pyramidal, small energy barrier to invert pyramidal geometry
      1. planar – 5% s character in orbital containing electron
      2. ESR – orbital connecting to electron and 13C – little significant s character
      3. EWG increase s character, why?

 

* 1. normally very reactive with short lifetimes
  2. If they don't react with closed shell molecules, they decay by termination (coupling and disproportionation: examples)

 

* 1. acids, bases and polar solvent have minor affect
  2. stabilization
     1. alkyl substitution, (methyl < primary < secondary < tertiary)



* + - 1. hyperconjugation



* + - 1. greater reduction in steric interaction when radical forms
    1. resonance stabilization (allyl, benzyl, heteroatom) – related BDE

, 

* + 1. steric hindrance inhibit radical combination

non planar rings in triphenylmethyl radical



1. Radical formation
   1. Electron transfer
      1. Chemical reduction 



, 



* + 1. Electrolytic reduction



* + 1. oxidation: 
       1. , also works with Ce+4, Mn+3 and Ag+2
       2. Electrolytic oxidation:



* 1. thermal cleavage – weak bonds: cumulated lone pairs, stabilized products, organometallics for electronegative metal





* 1. photolysis
     1. cumulated lone pairs: Br2, , HOX,
     2.  electrons: alkenes and carbonyls



1. Reactions of radicals
   1. atom abstraction - usually monovalent (H or halogen)
      1. dependent on bond energies, TS can have polar character
      2. 
      3. 
      4. rates can be estimated where abstraction is rate determining step



broken formed

BDE CH3CH2-H (98) Br-H (88)

CH3CH2-H (98) F-H (136)

Ea for Br = 13.2 kcal/mol, H\* = 12.6 kcal/mol

Ea for F = 0.3 kcal/mol, H\* = -0.3 kcal/mol

* + 1. exothermic processes are diffusion controlled, barrier estimated from activation energy (2-5 kcal in solution)

endothermic barrier estimated from bond energy difference and reverse barrier (2-5 kcal)

* 1. fragmentation



* 1. Addition
     1. To other radicals: 
     2. To  bonds: 





* + 1. To empty orbitals:



1. destruction of radicals
   1. preceding reactions have “exchanged” radicals
   2. coupling (recombination):
   3. disproportionation: 
   4. oxidation: , M+n = Pb+4, Ce+4, Mn+3, Ag+2
2. chain reactions: path combination
   1. example substitution: methane halogenation
   2. propagation (chain reaction) can occur many times per initiation: 106 for Cl

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Enthalpies of propagation steps | | | | |
| step | F | Cl | Br | I |
| 1 | -31 | 2 | 17 | 34 |
| 2 | -70 | -26 | -24 | -21 |

initiation 

propagation 



termination 

* 1. termination rate constant is fast, but it is bimolecular and radical concentrations are low
  2. propagation steps can compete because substrate concentration is high
  3. feasibility determined by propagation steps, e. g. for methane bromination and iodination does not occur at an appreciable rate (rate related to enthalpy of propagation step, difference in bond energies
  4. at 25 C, bromination of alkanes (per H): R3C-H (1600) > R2CH-H (80) > RCH2-H(1)
  5. Chlorination of alkanes (per H): R3CH (6.7) > R2CH2 (4.4) > RCH3 (1)
  6. polar effects- chlorination more sensitive than bromination
     1. the -CH bonds are weakest but are also relatively electron deficient
     2. the chlorine radical is electrophilic so it avoids the elecron deficient -CH



Chlorination of chlorobutane: 

1. radical addition
   1. HBr addition:



|  |  |  |
| --- | --- | --- |
| H (kcal/mol) of X addition and H abstraction steps | | |
|  | X• + CH2=CH2 | XCH2CH2• + HX |
| HF | -45 | 37 |
| HCl | -26 | 5 |
| HBr | -5 | -11 |
| HI | 7 | -27 |

For halogen acids only HBr is exothermic for both reactions

* 1. RSH, Br3CH, Cl3CH are the same mechanism
  2. BrCCl3, and CCl4 have a carbon or silicon radical initiation



* 1. X2



* 1. Polymerization
     1. Chain length determines concentrations and rates of steps
     2. Branching can occur from H abstraction



1. addition to nitroso or nitrone compounds
   1. stable radicals are formed
   2. two-atom 3-electron bonds, what are MO’s for NO?



1. autooxidation

 initiation (source of ROOH?) OH!!!



 propagation

 propagation

 termination

1. inhibitors - abstraction or addition forms unreactive radicals



1. selected reactions
   1. hydroxylation arenes



* 1. silicon hydride (or tin hydride) reduction of alkyl halides.???









* 1. diacyl peroxide reduction, catalytic in copper (only for R = alkyl)
     1. cation may rearrange or react with added nucleophile









* 1. rearrangements
     1. phenyl migration, delocalization provide low energy



* + 1. Alkyl radical rearrangements rare! Compare carbon cation transition state or intermediate structure
  1. Dissolving metal reduction
     1. olefins, alkynes, aromatics
     2. note that C radicals oxidize electropositive metals
     3. RX + 2Na R2



1. esters, aldehydes and ketones (acyloin)