

11: Free Radical Substitution and Addition Reactions

11.1 Free Radicals and Free Radical Reactions

Free Radicals (11.1A)

Halogen Atoms

Alkoxy Radicals

Carbon Radicals

11.2 Halogenation of Alkanes with Br₂

Bromination of Ethane (11.2A)

Mechanism

Initiation Step

Propagation Steps

The CH₃-CH₂· Radical

Radical Chain Reactions (11.2B)

Propagation Steps Repeat

Many Chains Occur Simultaneously

Termination Reactions (11.2C)

Combination Reactions

Disproportionation Reactions

Polybromination (11.2D)

11.3 Alternate Bromination Sites

General Mechanism for Propane Bromination (11.3A)

Origins of 1-Bromopropane and 2-Bromopropane (11.3B)

Propagation Reactions

Termination Reactions

Polybromination

11.4 Relative Reactivity of C-H Hydrogens

C-H Bond Strengths (11.4A)

Bond Strengths

C-H Bond Strength and Alkane Structure

Relative Reactivities of C-H's

Radical Stability (11.4B)

Relative Stabilities of Alkyl Radicals

Origin of Radical Stability Order

11.5 Alkane Halogenation with Cl₂, F₂, or I₂

Chlorination (11.5A)

Relative Product Yields in Chlorination and Bromination

Cl· is More Reactive and Less Selective than Br·

Correlation Between Reactivity and Selectivity

Fluorination and Iodination of Alkanes (11.5B)

(continued)

11.6 Radical Additions to Alkenes

H-Br Addition (11.6A)

H-Br Addition Mechanism (11.6B)

Propagation

Initiation

Termination

H-Br Addition Regiochemistry (11.6C)

Radical versus Electrophilic Addition

Radical Stability

Steric Effects

H-Br Addition Stereochemistry (11.6D)

H-I, H-Cl, and H-F Additions are Electrophilic (11.6E)

Radical Addition of Br₂ or Cl₂ (11.6F)

Mechanism

Competitive Substitution

F₂ and I₂

Appendix A

11.7 Alkane Halogenation with Other Reagents

t-Butyl Hypohalites (11.7A)

Mechanism

t-Butyl Hypohalite Preparation

N-Bromosuccinimide (11.7B)

Overall Reaction

Mechanism

Appendix B

11.8 Halogen Atom Reactivity and Selectivity

Reaction of Methane with X[•] (11.8A)

Structural Changes During Reaction

Energy Changes During Reaction

Exothermic and Endothermic Reactions

Transition States or Activated Complexes (11.8B)

Energy Maximum and Transition State

Reaction Rates and Activation Energy

Reactivity and Activation Energies

An Explanation for Selectivity-Reactivity Correlation (11.8C)

Resemblance of Transition States to Reactants and Products

Radical Character in the Transition State

The Hammond Postulate