

## CHAPTER OUTLINE

9.1 Structure and Stability of Free Radicals

9.2 Bond Dissociation Energies

### Free Radicals and Biology

9.3 Chlorination of Methane

9.4 Mechanism of Methane Chlorination

### Halogenated Hydrocarbons and the Environment

9.5 Halogenation of Higher Alkanes

9.6 Chlorofluorocarbons and the Environment

9.7 Free-Radical Addition of Hydrogen Bromide to Alkenes

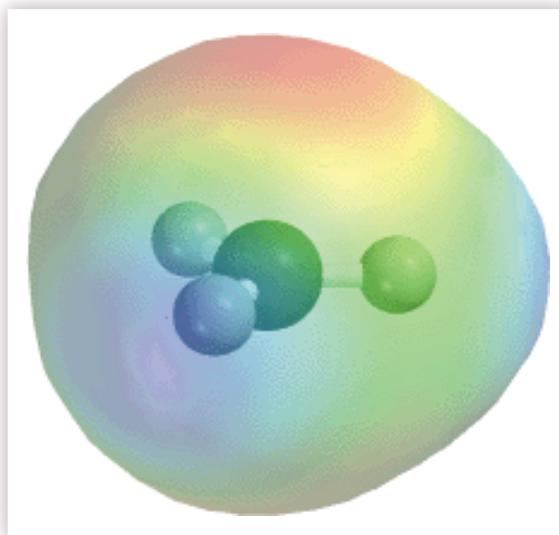
9.8 Polymerization of Alkenes

### Diene Polymers

### Learning Objectives

9.9 Summary

### Additional Problems



# CHAPTER 9

## FREE RADICALS

Several of the reactions we have examined proceed by multistep mechanisms that involve carbocation intermediates. These reactions include

Preparation of alkyl halides from alcohols (Chapter 3)

Dehydration of alcohols (Chapter 4)

Electrophilic addition to alkenes (Chapter 5)

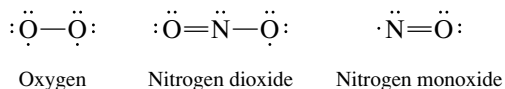
Electrophilic aromatic substitution (Chapter 6)

Unimolecular ( $S_N1$ ) nucleophilic substitution (Chapter 8)

In this chapter we will explore a different type of reactive intermediate—a neutral species known as a free radical.

### 9.1 STRUCTURE AND STABILITY OF FREE RADICALS

**Free radicals** are species that contain unpaired electrons. The octet rule notwithstanding, not all compounds have all of their electrons paired. Oxygen ( $O_2$ ) is the most familiar example of a compound with unpaired electrons; it has two of them. Compounds that have an odd number of electrons, such as nitrogen dioxide ( $NO_2$ ), must have at least one unpaired electron.



Nitrogen monoxide (“nitric oxide”) is another stable free radical. Although known for hundreds of years, NO has only recently been discovered to be an extremely important