Radicals and Hydroxy Radical Reactions in Troposphere

Examples of ground state radicals:

1. H atom: 1 electron
2. O and O_2: unpaired electrons in orbitals: QM reason
3. OH: hydroxy radical: 7 valence electrons
4. OOH: peroxyl radical
   - Very reactive: 1 $H\cdot$ away from H_2O, one electron away from OH^-
   - Very important in tropospheric chemistry
5. NO: Nitric Oxide, ll valence electrons
6. NO_2: Nitrogen dioxide, 17 valence electrons
7. NO_3: Nitrate radical
8. $R-CH_2\cdot$: alkyl radical
   - $R=$ anything. Example: $R=H \Longrightarrow CH_3\cdot$, methyl radical
   - Reacts rapidly with O_2
9. $R-CH_2-O-O\cdot$: alkyl peroxyl radical
   - Formed in:

$$RCH_2\cdot + O_2 \rightarrow R-CH_2-O-O\cdot$$

10. $R-CH_2-O\cdot$: alkyl oxyl radical
    - Typical reaction:

$$R-CH_2-O\cdot + O_2 \rightarrow R-COH + \cdot O-O-H$$

Hydroxy Radical Chemistry: OH is main oxidizing agent which breaks down organic pollutants in troposphere

- Examples: CH_4 and toluene
- How is OH produced? Major source:Photolysis of ozone

$$\begin{aligned} &O_3 \xrightarrow{h\nu} O_2^*(s) + O^*(^1D) \\ &O^*(^1D) + H_2O \longrightarrow 2\ \cdot OH \quad \text{small } \phi_r \\ &O^*(^1D) + M \longrightarrow O + M + \text{heat} \end{aligned}$$

- Minor sources: Photolysis of termination reaction products

$$\begin{aligned} &H_2O_2 \xrightarrow{h\nu} 2\ \cdot OH \\ &HONO \xrightarrow{h\nu} \cdot OH + NO\cdot \end{aligned}$$

- Where does the O_3 come from?

$$NO_2 \xrightarrow{h\nu} NO + O(^3P) \tag{1}$$
$$O + O_2 \xrightarrow{M} O_3 \tag{2}$$

- Where does the NO_2 come from?

$$N_2 + O_2 \xrightarrow{\Delta} 2NO$$
$$NO + \cdot O - O - H \longrightarrow NO_2 + \cdot OH \tag{3}$$

- Where does the OOH come from?

$$H\cdot + O_2 \xrightarrow{M} \cdot O - O - H \tag{4}$$

- Source of $H\cdot$?

$$\cdot O - H + CO \longrightarrow CO_2 + \cdot H \tag{5}$$

- The net reaction resulting from processes is:

$$CO + 2O_2 \xrightarrow{h\nu, NO_x, \cdot O-H} CO_2 + O_3$$

  - Photoinitiated in step 1
  - Oxidize CO to produce ozone
  - Continuous conversion between OH and NO_2

Classification of OH reactions

1. Addition reactions: unsaturated compounds
   - Example: $OH + CO \longrightarrow CO_2 + OOH$
2. Abstraction reactions: OH pulls off a hydrogen atom
   - Example: $CH_4 + OH \longrightarrow CH_3 \cdot + H_2O$

- Both addition reactions and H abstraction can occur with same molecule?
  - Which dominates? Depends on reaction rates-details of conditions and molecule.

The art of synthesis: rules of thumb

1. If compound is unsaturated, then OH addition occurs
2. If compound has an H that OH can abstract in an exothermic reaction, this generally occurs
   - Bond strengths important: $O - H$ vs. $C - H$
   - Both processes depend on relative strengths of the bonds in the compound compared to the $O - H$ bond. Reactions generally go downhill in energy.