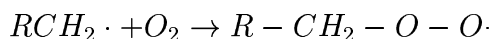


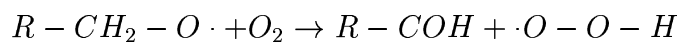
Radicals and Hydroxy Radical Reactions in Troposphere

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 : peroxy radical
 - Very reactive: 1 $H\cdot$ away from H_2O , one electron away from OH^-
 - Very important in tropospheric chemistry
5. NO : Nitric Oxide, 11 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: $R = H \implies CH_3\cdot$, methyl radical
 - Reacts rapidly with O_2
9. $R - CH_2 - O - O\cdot$: alkyl peroxy radical
 - Formed in:

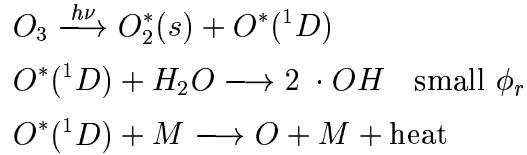


10. $R - CH_2 - O\cdot$: alkyl oxy radical
 - Typical reaction:

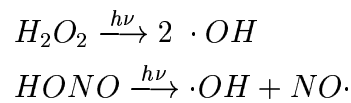


Hydroxy Radical Chemistry: OH is main oxidizing agent which breaks down organic pollutants in troposphere

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



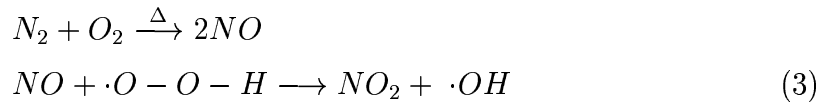
- Minor sources: Photolysis of termination reaction products



- Where does the O_3 come from?



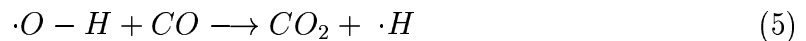
- Where does the NO_2 come from?



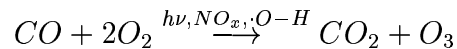
- Where does the OOH come from?



- Source of $H \cdot$?



- The net reaction resulting from processes is:



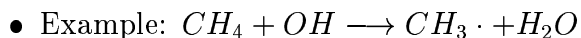
- Photoinitiated in step 1
- Oxidize CO to produce ozone
- Continuous conversion between OH and NO_2

Classification of OH reactions

1. Addition reactions: unsaturated compounds



2. Abstraction reactions: OH pulls off a hydrogen atom



- 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



- Both processes depend on relative strengths of the bonds in the compound compared to the $O - H$ bond. Reactions generally go downhill in energy.