

# Smog and Photochemical Pollution

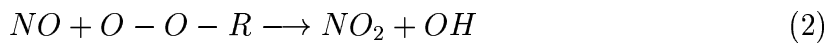
- First observed in Los Angeles
  - Transportation emissions trapped in air basin
  - Characterized by reddish-brown haze and toxic chemicals: Ozone
  - Hot weather
  - Introduction of  $NO$  and hydrocarbons ( $RH$ ) shifts natural balance of  $NO_x/O_3$  and  $OH$  cycles

## Daily Cycle

1. Cars start in morning: provide heat



2. Oxidation of  $NO$  later in morning



3. Photolysis of  $NO_2$



4. Formation of ozone



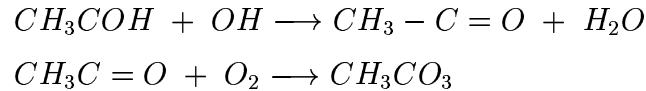
5. Photolysis of ozone to form  $OH$



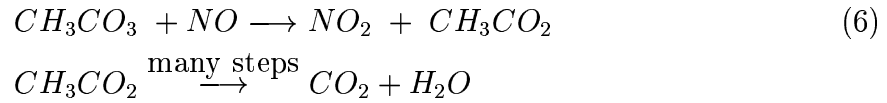
6. Formation of hydrocarbon radicals  $\implies$  interaction with 2

- Late in day, 3 slows down toxic compounds such as aldehydes, peroxyacetylnitrate (PAN) build up.

**Formation of PAN:** aldehyde breakdown in presence of  $NO_2$  radical



then either



or



can be important.

- During day, photolysis of  $NO_2$  keeps  $[NO_2]$  small, so path (6) dominates.
- Late in day,  $[NO_2]$  builds up and less  $NO$  is present (shift in equilibrium), so path (7) becomes significant.

## Summary of Smog Cycle

**Early in day:**

- Peak production of  $NO$  and  $RH$  early in morning: morning commute
- Peroxy radical oxidation of  $NO$  to form visible  $NO_2$

**Noon-early afternoon:**

- Hydrocarbons converted to aldehydes, then broken down to  $CO_2$  and  $H_2O$
- Ozone production from  $NO_2$  photolysis

**Late daylight hours:**

- Fewer UV rays for photolysis,  $O_3$  and  $NO_2$  build up
- Less  $NO$  and more  $NO_2$ , so aldehyde oxidation less dominant
- $NO_2$  radical combines with organic radicals in a termination reaction to make toxic compounds like PAN
- Toxic compounds stable until morning sunlight photolyses them: reservoir gases for  $NO_2$  and organic radicals.

**Measurement of pollution levels:** Concentrations of toxic compounds like aldehydes and *ground-level ozone* are measured.

- Set standards: World Health Organization (WHO)
  - WHO standard for “safe” air: 100 ppb (parts per billion)
  - USA standard: 120 ppb
  - Canadian standard: 82 ppb
- Peak ozone level in L.A. in 1970’s: 680 ppb
  - Typically around 300 ppb now: How?
- Problem worst in Mexico City: Exceed WHO standards 310 days/yr
  - Thousands of premature deaths annually in Mexico City due to respiratory problems: Oxidation of tissues and lung disease
  - Also very bad in Athens and Rome
- Transport of pollutants affects rural areas
  - Ex. Southwestern Ontario farmland pollution from Lake Erie industry.

## What to do?

Photochemical pollution requires:

1. Heat-little can be done
2. Hydrocarbons
3.  $NO_x$

**Mimimisation of role of Hydrocarbons:**

1. Reduce concentrations of very active hydrocarbons:
  - Large hydrocarbons with weak  $C - H$  bonds:  $H$ -abstraction
  - Unsaturated  $RH$  such as alkenes:  $OH$  addition
  - Aromatic compounds: stabilization effects
2. Major problem: gasoline and petroleum products
  - Home furnaces, power plants, industry

- Vapor locks on gas station and limit industrial leakages
- Natural sources: Terpenes (unsaturated) from trees and plants
  - Conifers: pinene (in needles) and limonene account for 70% of  $RH$  in Atlanta
  - Deciduous trees and shrubs: isoprene (rubbery sap)
- Best approach: avoid petroleum fuels: alternative energy sources like *biodiesel*
  - Biodiesel: rape methyl ester (RME) produced from rapeseed oil (vegetable oil) can be used directly in diesel engines. Also sunflower oil or Soya oils can be converted to fuel.
    - \* Reduces  $RH$  and  $CO$  emissions by 50%,  $NO_x$  by 10%.
    - \* Fewer deposits and less wear on engine
    - \* Accounts for 15% of Austrian diesel market
    - \* Used in taxi fleets and buses in Berlin, Zurich, Bologna and Lake Como
    - \* Used as a heating fuel in the German parliament building (Reichstag): provides enough heat for 50,000 homes
    - \* Growing rapeseed plant provides  $CO_2$  sink
- Reformulate fuels to minimize photochemical pollution

### Formulations of gasoline:

- Burning fuel involves radical chemistry:  $O_2$  combines with radicals created by spark from spark plug
  - Compression of air/fuel also heats mixture which can produce radicals: called pre-ignition or “knocking”
  - Temperature of radical generation depends on mixture of compounds in gasoline
    - \* Branched chain hydrocarbons more resistant to radical generation: iso-octane (octane rating)
    - \* Companies tried lead additives which pollutes and dirties engine, and aromatic compounds (carcinogenic)
  - New attempt: “oxygenates” additives like methyl-tertiary-butyl-ester (MTBE)
    - \* Clean burning leads to less  $CO$  and unburned  $RH$ , but leads to more  $NO$  due to hotter engine

### $NO_x$ emissions and emissions controls: Key

- 3-way catalytic converter: Large effect in California

- Surface catalysis on Rh and Pt/Pd surfaces greatly limits  $NO_x$ ,  $CO$  and  $RH$  emissions
- Releases  $CO_2$ ,  $N_2$ ,  $H_2O$  and  $O_2$ : mainly benign products