# Photochemistry of Smog and Secondary Aerosol formation

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# Outline

- Introduction
- Mechanism of ozone formation
- Secondary aerosol formation
- Gas and liquid-phase production of SOA

# Introduction

- Smog is a mixture of Smoke and Fog

- Smog type:

  -London or the Classical Smog

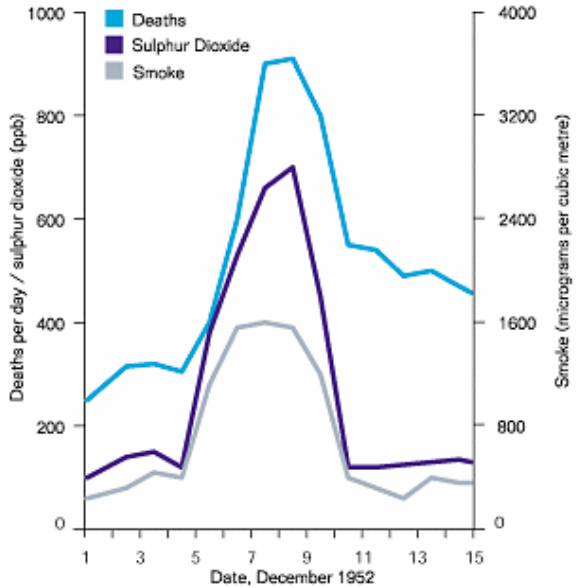
  -Los Angeles or The Photochemical Smog

# London Smog

- Caused by huge amounts of coal burning in December 1952
- It is a sulfurous smog, a mixture of fog, soot, $SO_2$, PM, ...
- 100,000 were ill; 4000 people died prematurely of respiratory problems, followed by additional 8000 deaths

Some incidents of deaths associated with London type smog

| | | |
|---|---|---|
| 1930 | Meuse Valley, Belgium | 63 |
| 1948 | Donora, Pennsylvania | 20 |
| 1952 | London (5 days) | 4000 |
| 1962 | London | 700 |



# Los Angeles Smog

- New kind of smog
- First observed in Los Angeles
- Primary source - Velicle emissions

•High ozone level

•Low visibility (haze)

Los Angeles

# Ozone concentrations over Los Angeles and Boston

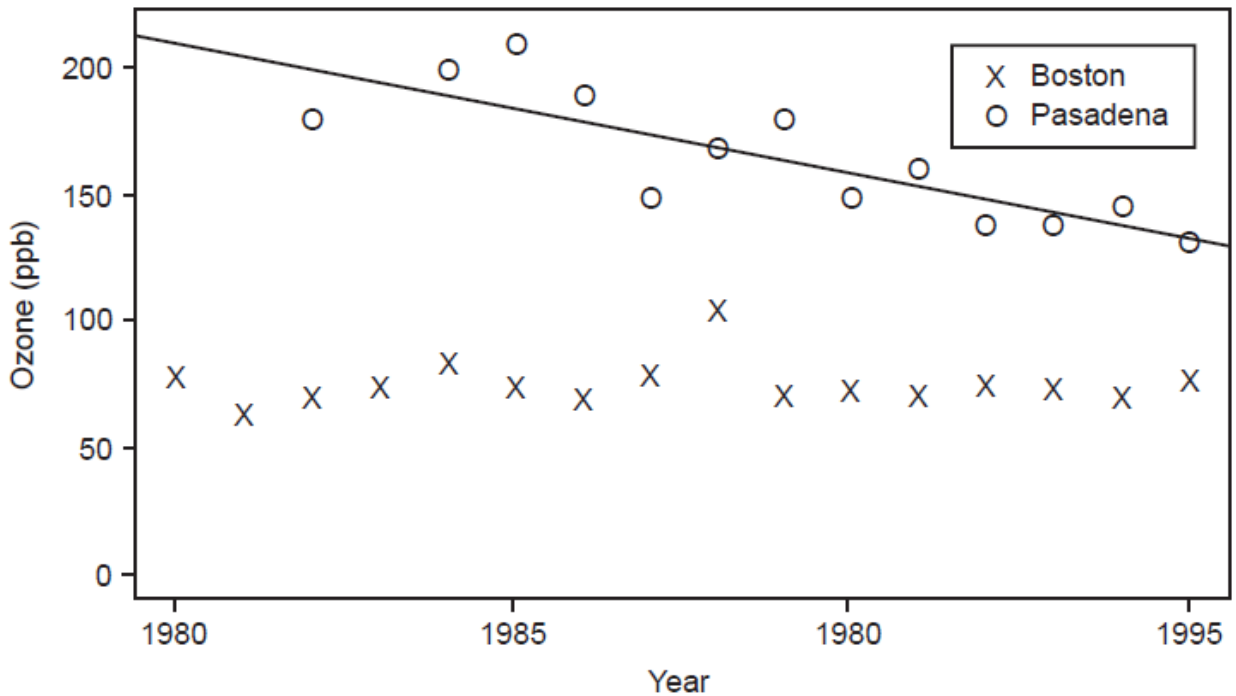
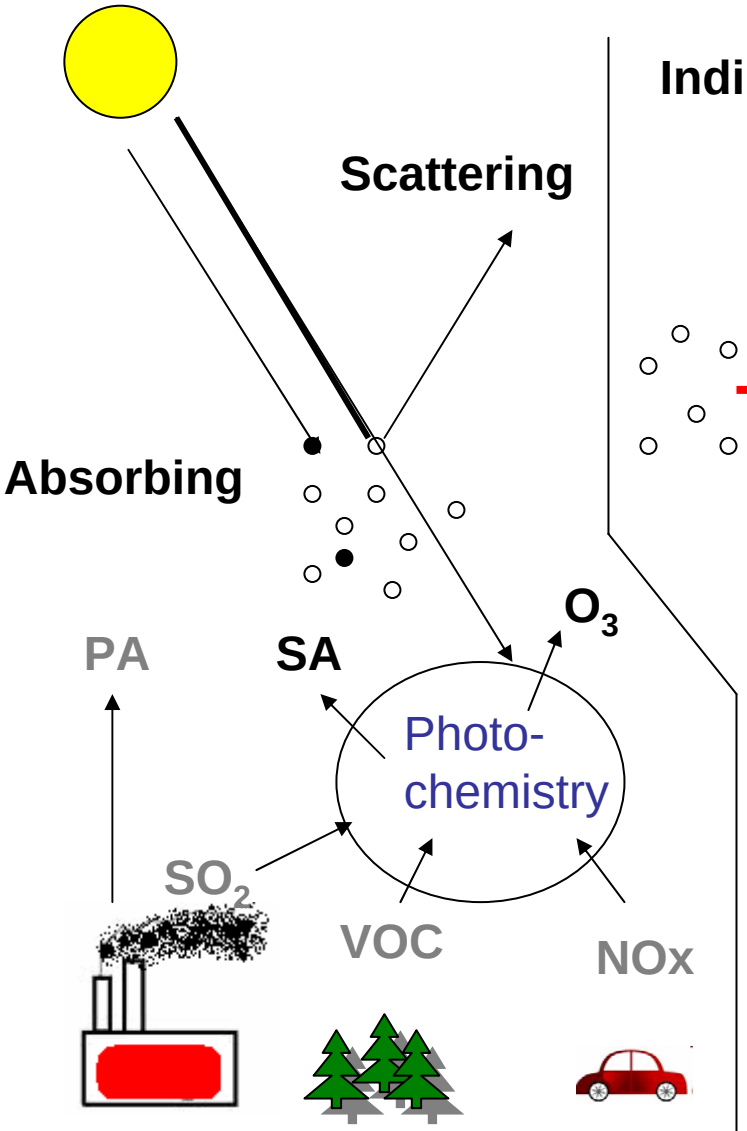
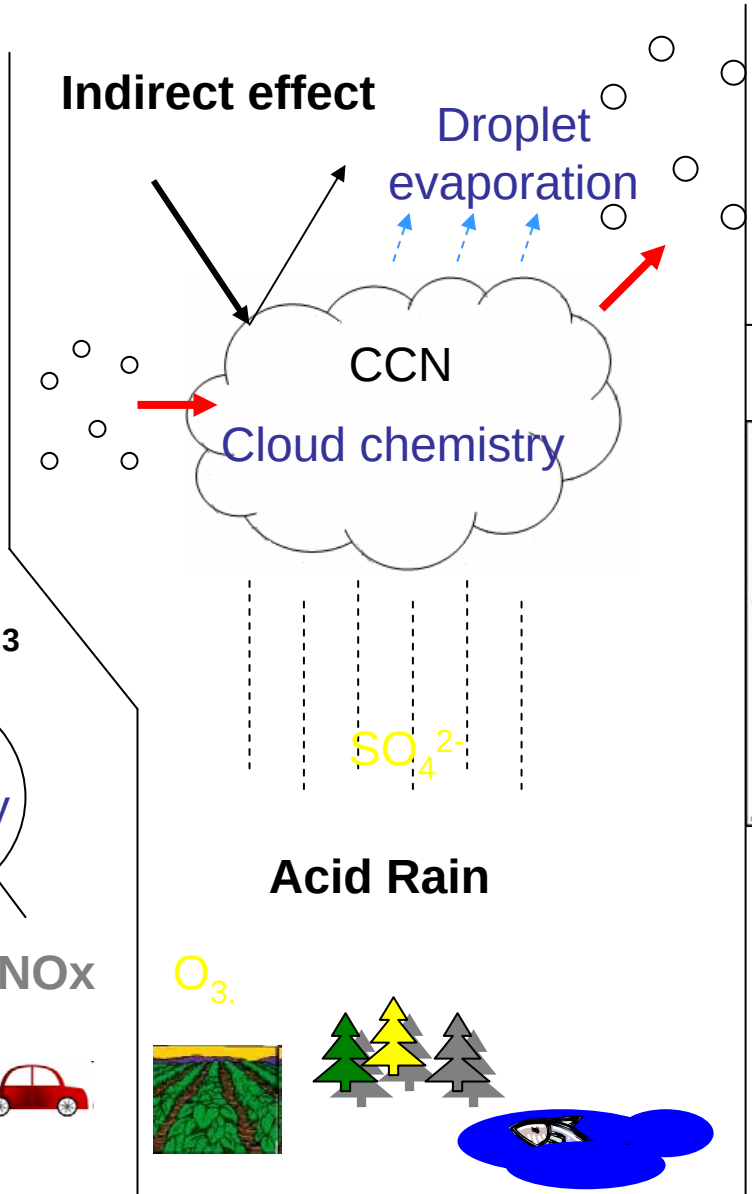



**Figure 12-5 Long-term trends in the 90th percentile summer afternoon concentrations of $O_3$ in Pasadena (Los Angeles Basin) and Boston for the period 1980-1995. There is a significant decreasing trend in Pasadena (the regression line is shown) but no significant trend in Boston. The high 1988 concentrations in Boston were due to anomalously stagnant weather over the eastern United States that summer.** From Fiore et al., op. cit.

# Interactions among air pollution emissions, photochemistry, radiation, and climate & health impacts

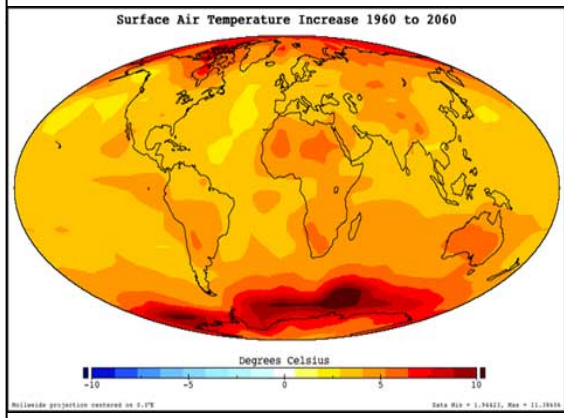


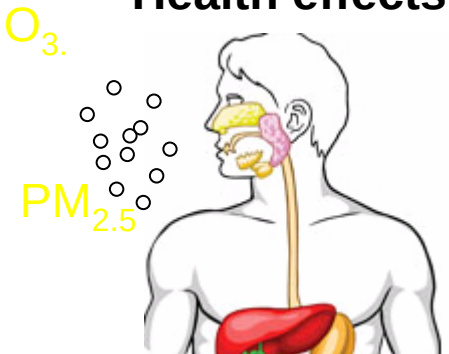




## Climate change



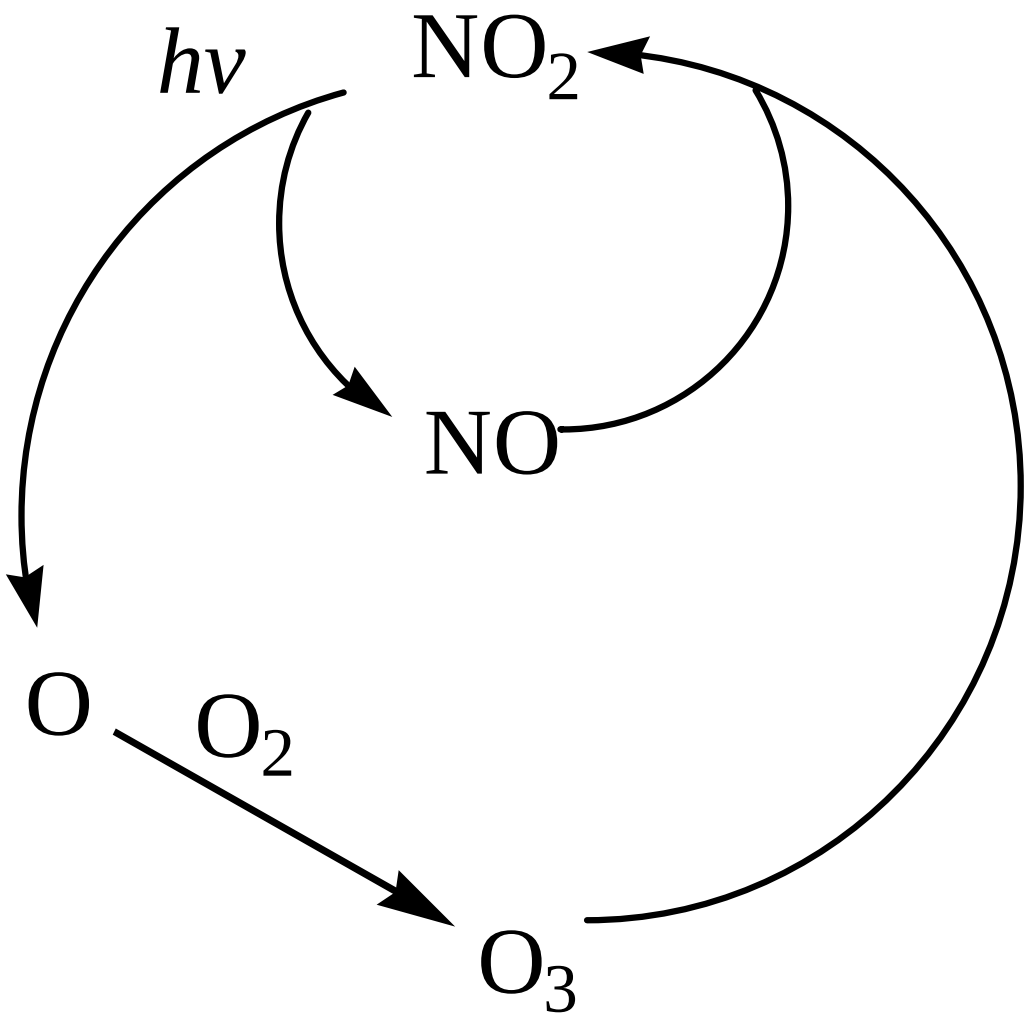

## Health effects



# Mechanism of photochemical smog

- Ozone formation
- Secondary aerosol formation

# Null cycle of NOx and $O_3$

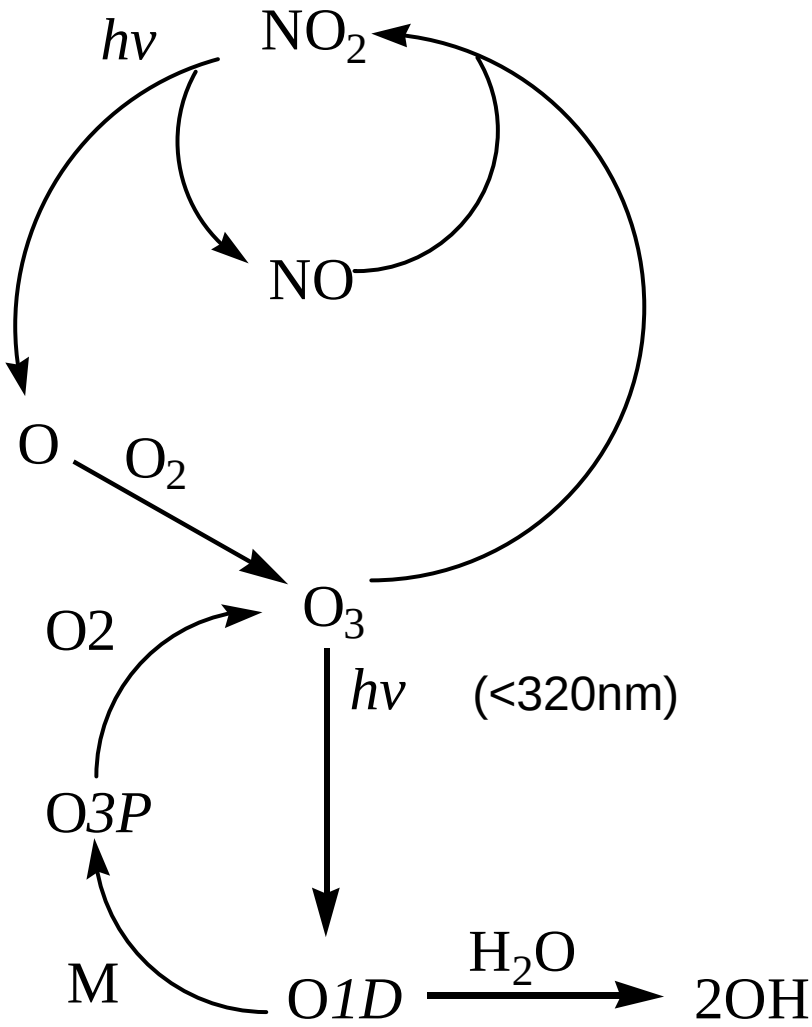



$O_3 + NO \rightarrow NO_2 + O_2$

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

# Production of OH radical




Dry:

$O_3 + h\nu \rightarrow O(1D) + O_2$

$O(1D) + M \rightarrow O(3P) + M$

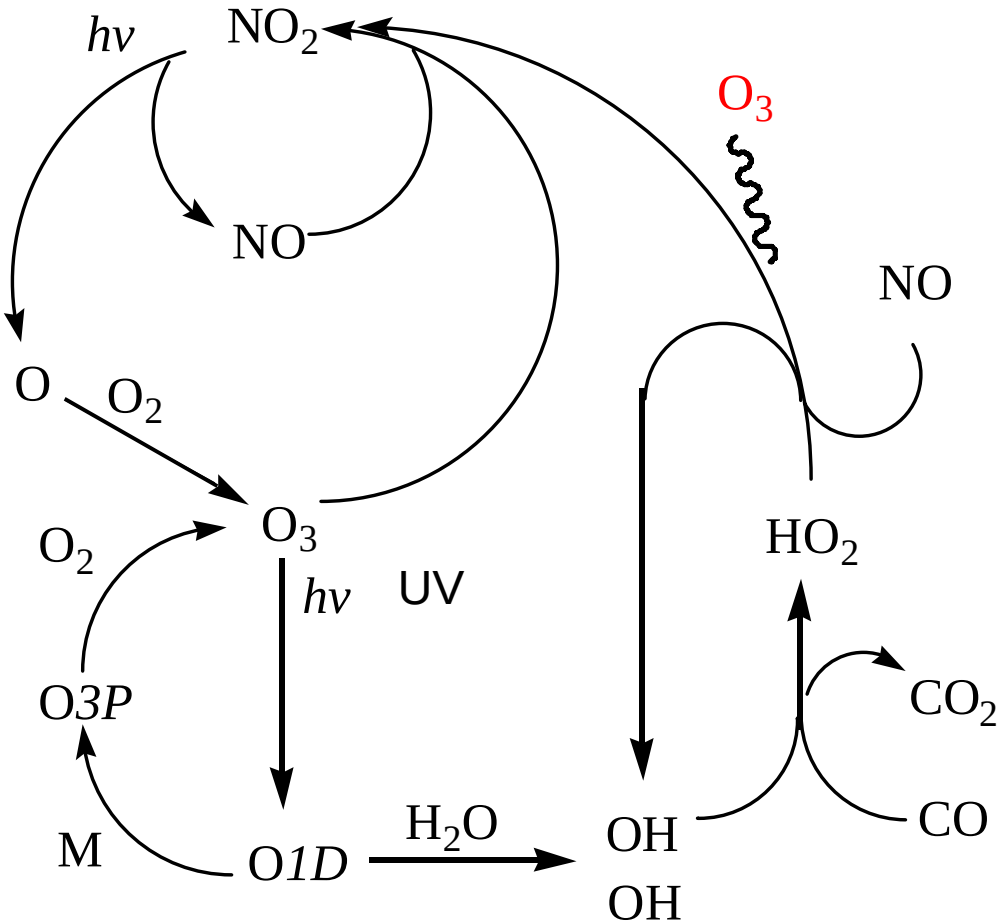
$O(3P) + O_2 \rightarrow O_3$

Humid:

$O(1D) + H_2O \rightarrow 2\ OH$

# Ozone accumulation

## (Case of CO)



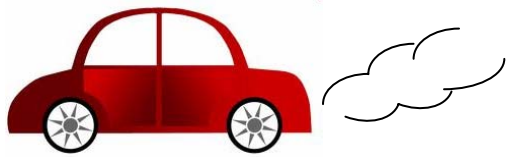

**Prerequisites for high ozone:**

- NOx: catalysts
- Photo: energy
- CO: fuel
- H2O: OH precursor

$CO + OH \rightarrow H + CO_2$

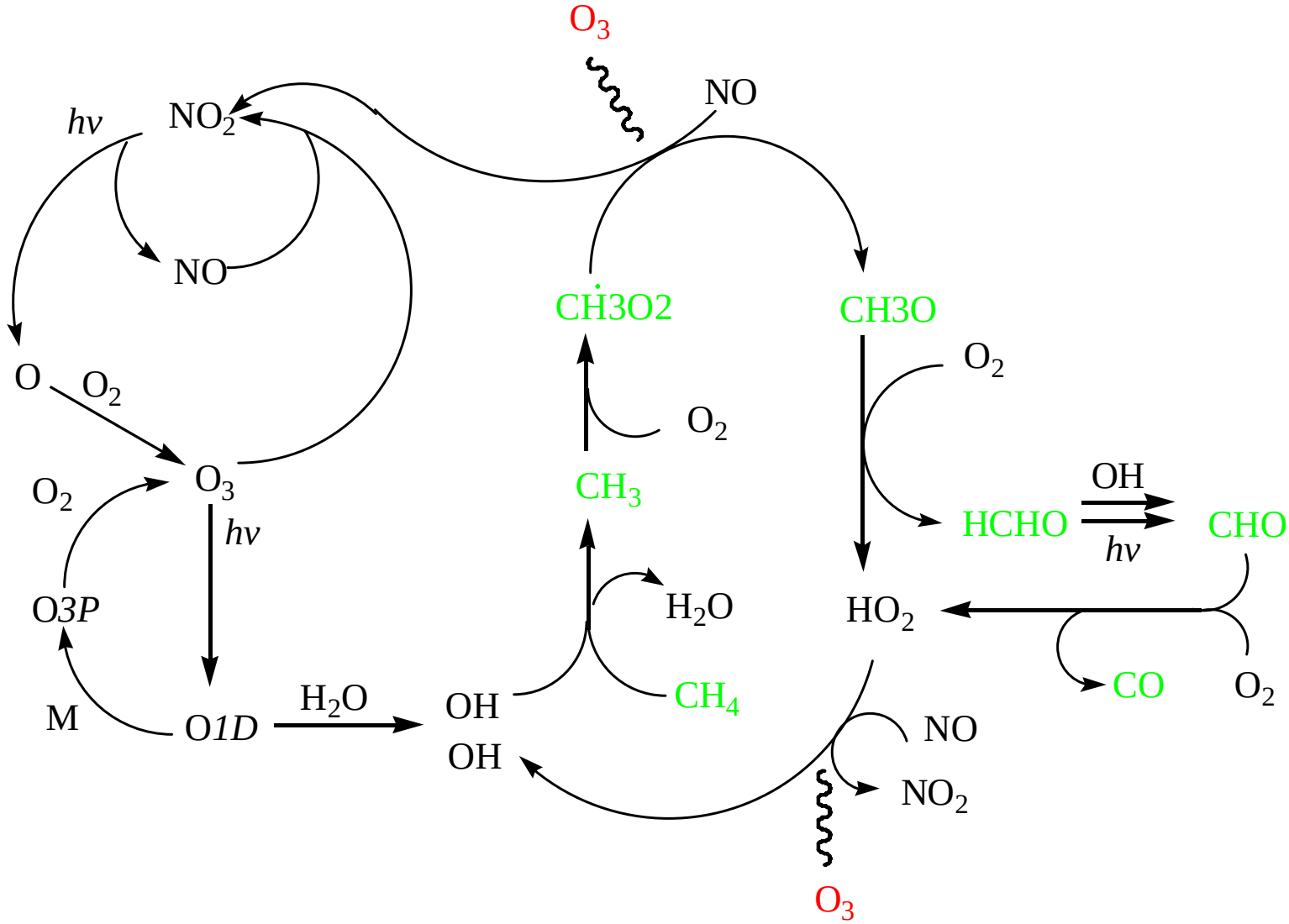
$H + O_2 \rightarrow HO_2$

NOx, CO, HC



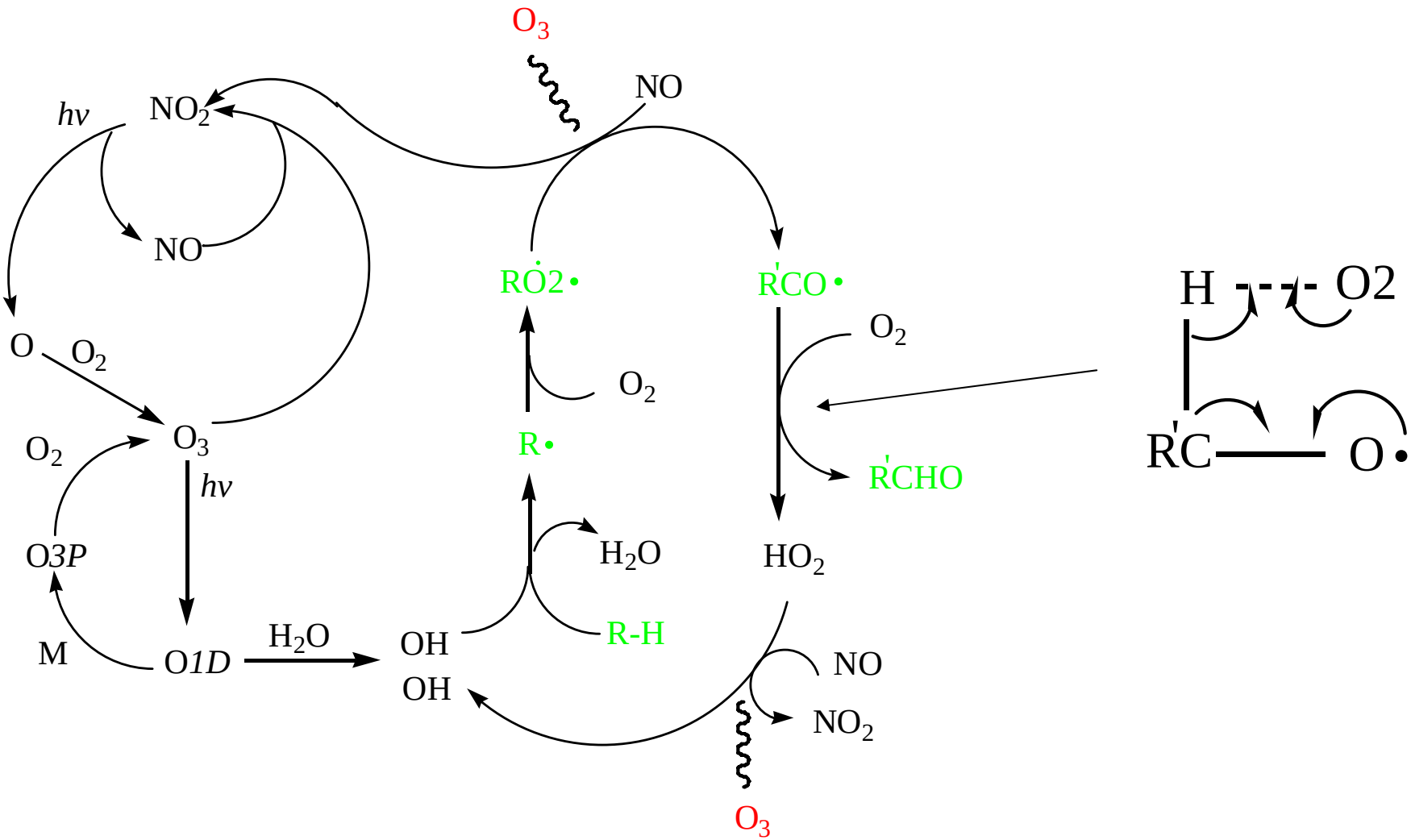
# Ozone accumulation

## (Case of $CH_4$)



# Ozone accumulation

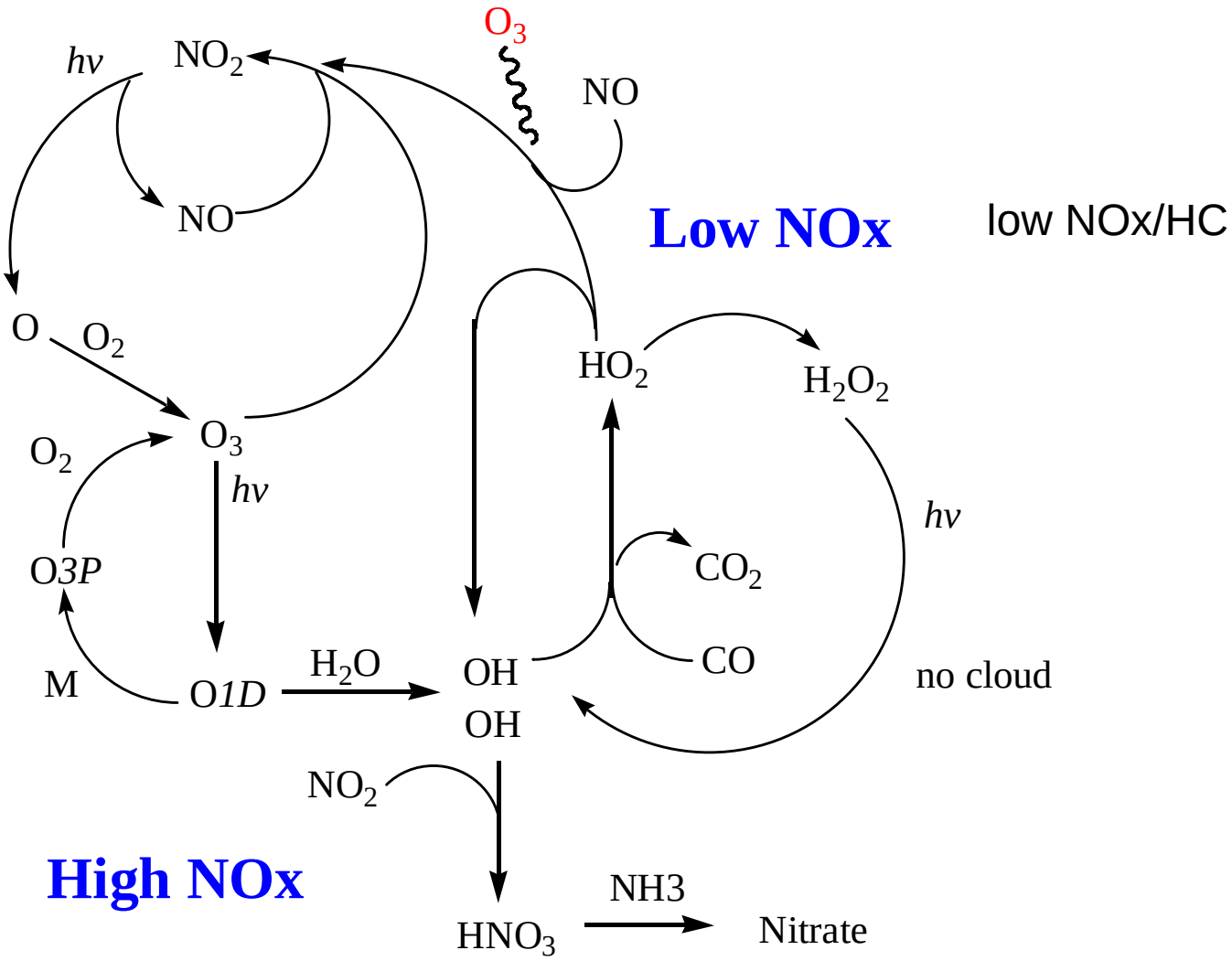
## (Case of HC)



# Secondary aerosol formation

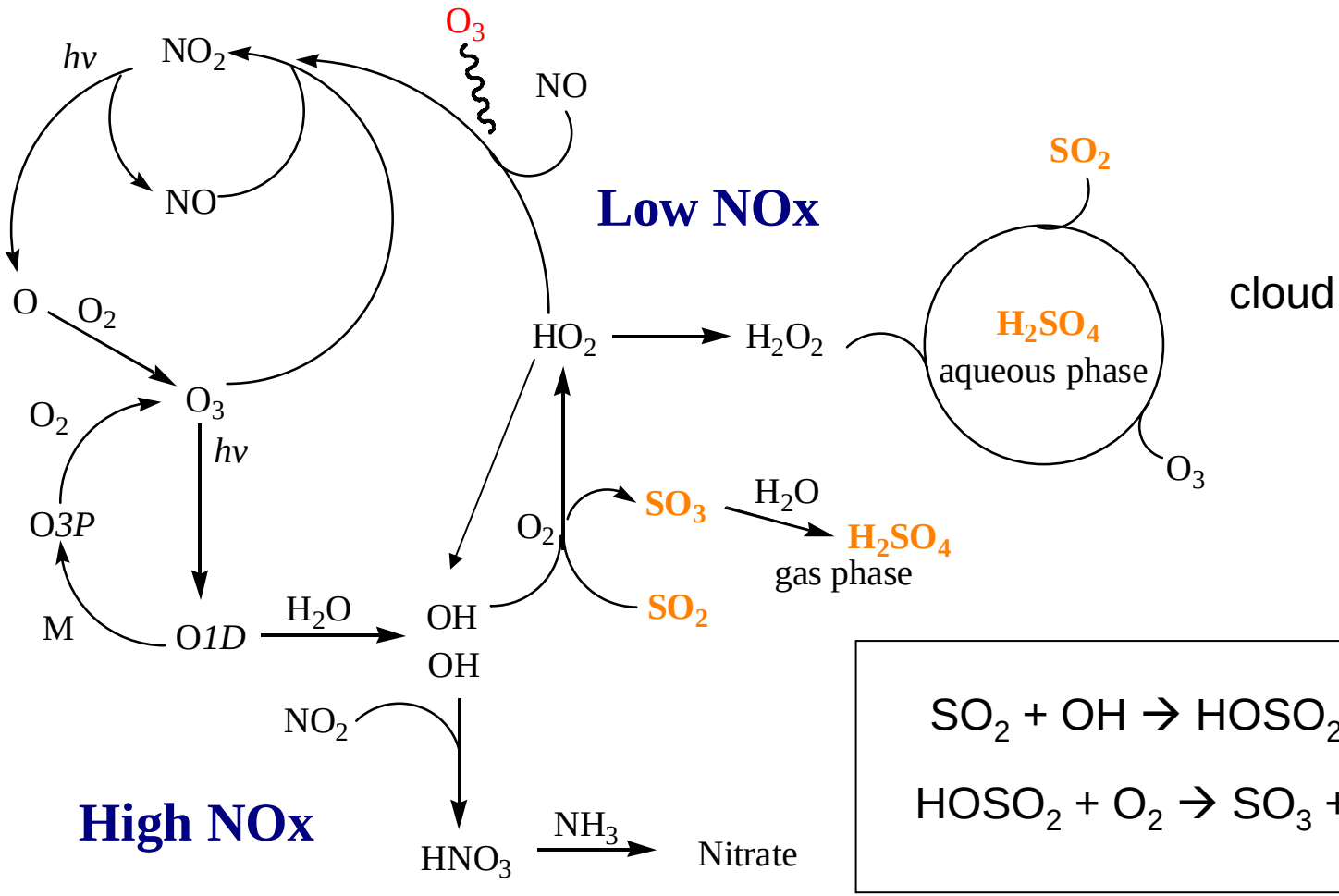
# Secondary Aerosol Formation

## (Nitrate)



# Secondary Aerosol Formation

## (sulfate)




$SO_2 + OH \rightarrow HOSO_2$

$HOSO_2 + O_2 \rightarrow SO_3 + HO_2$

# Secondary Aerosol Formation

## (oxidation of organics)

**HCHO (formaldhyde)**

**H2C=O + hv → HC=O + H**

**H + O2 → HO2**

**HC=O + OH → CO + HO2**

**CH2=CH2 (ethene)**

**CH2=CH2 + OH → OHCH2-CH2**

**OHCH2-CH2 + O2 → OHCH2CH2O2**

**OHCH2CH2O2 + NO → NO2 + OHCH2CH2O**

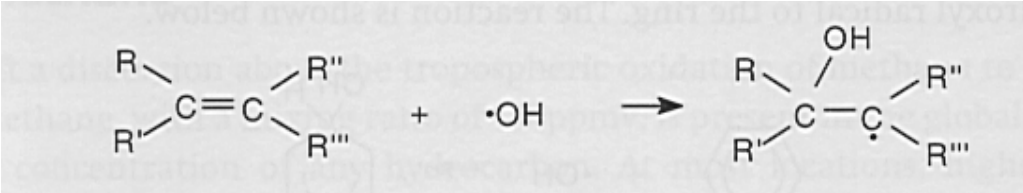
**OHCH2CH2O → H2C=O + ·CH2OH**

**O2 + ·CH2OH -> H2C=O + HO2**

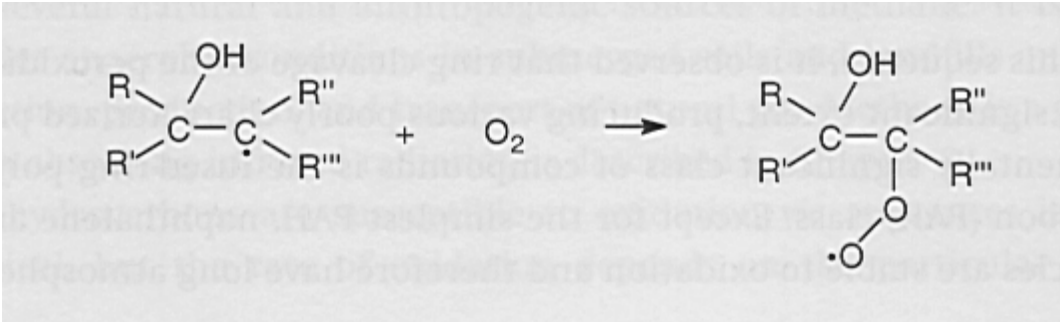
**These reactions produce a host of radicals which "fuel" the smog reaction process**

# Alkene + OH

**First OH radicals attack the electron rich double bond of an alkene**

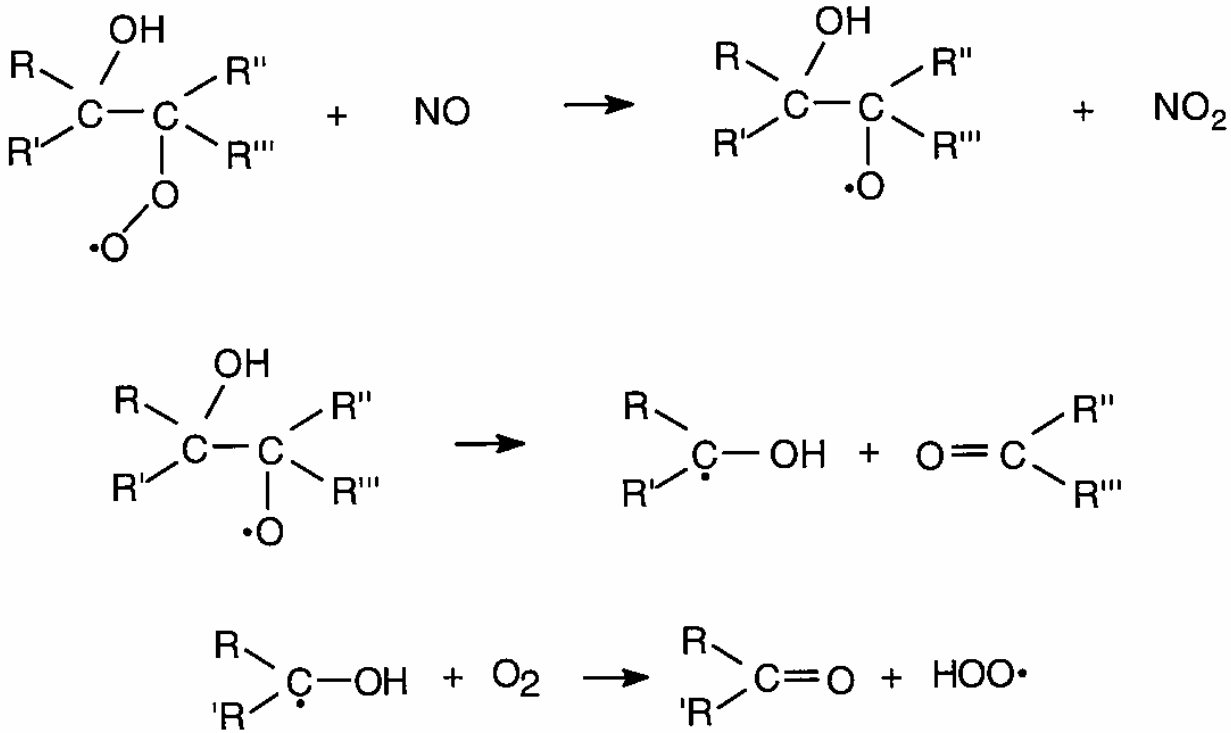



**Oxygen then add on the hydroxy radical forming a peroxy-hydroxy radical**

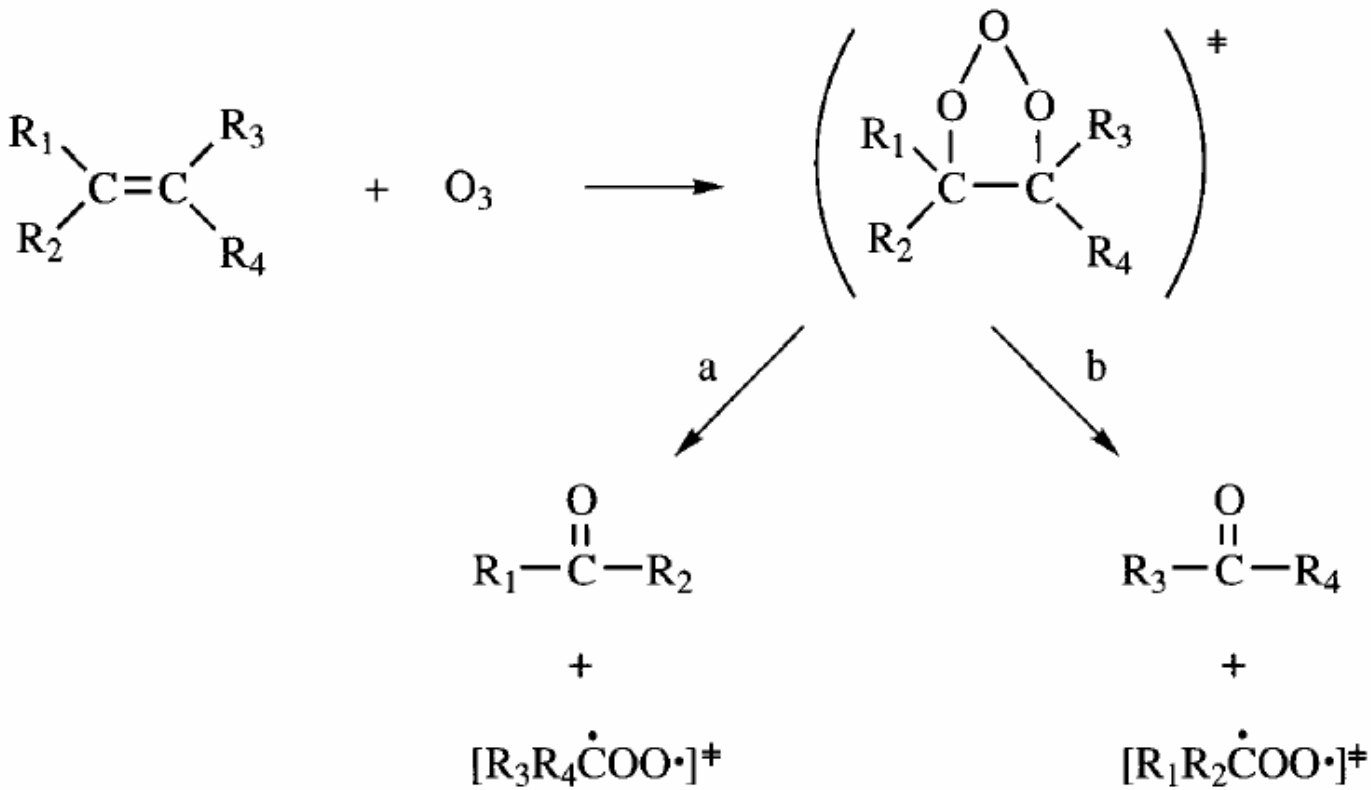



**the peroxy-hydroxy radical radical can oxidize NO to $NO_2$ ,just like $HO_2$ can**

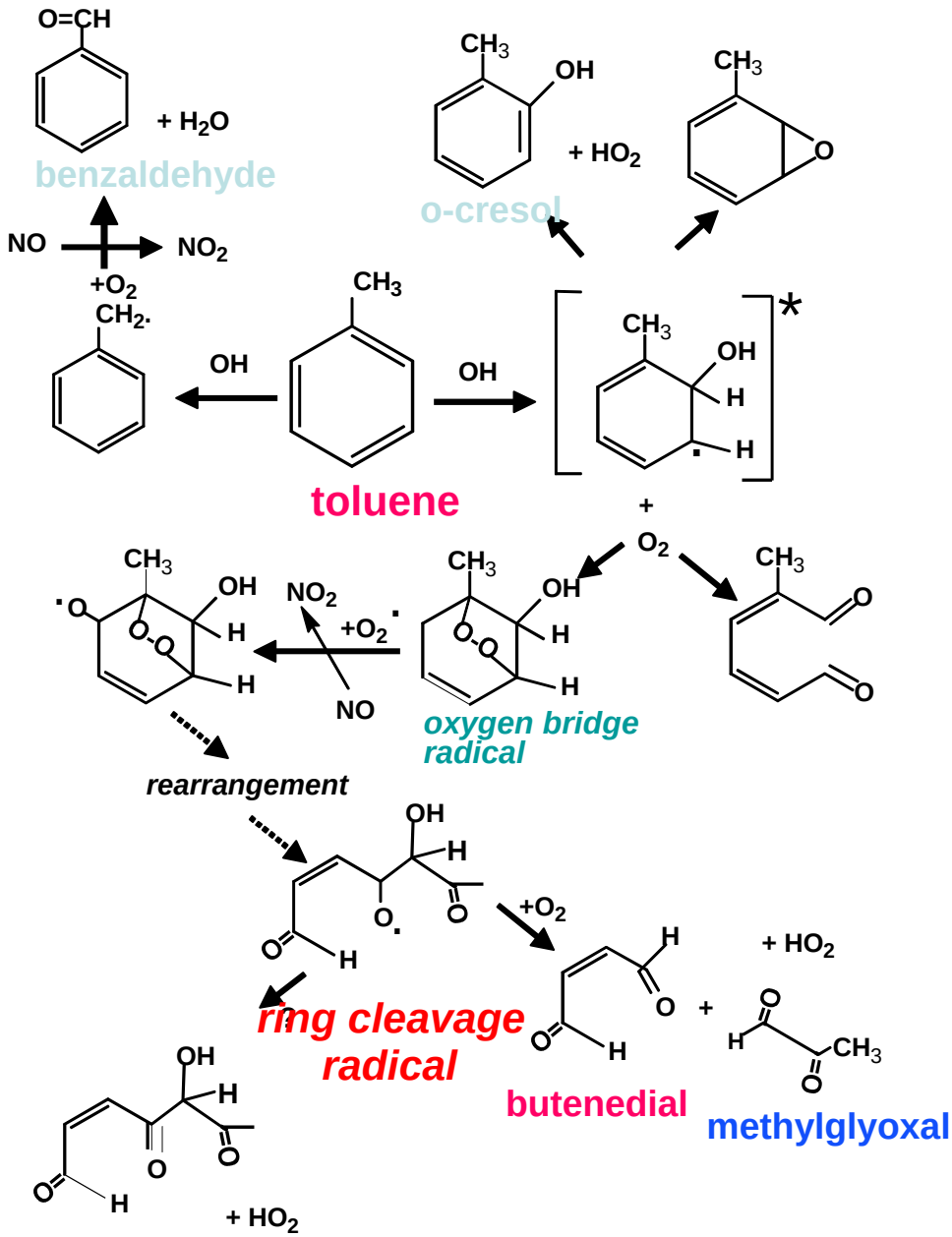
**Further reaction takes place resulting in carbonyls and $HO_2$ which now undergo further reaction; the process then proceeds…**



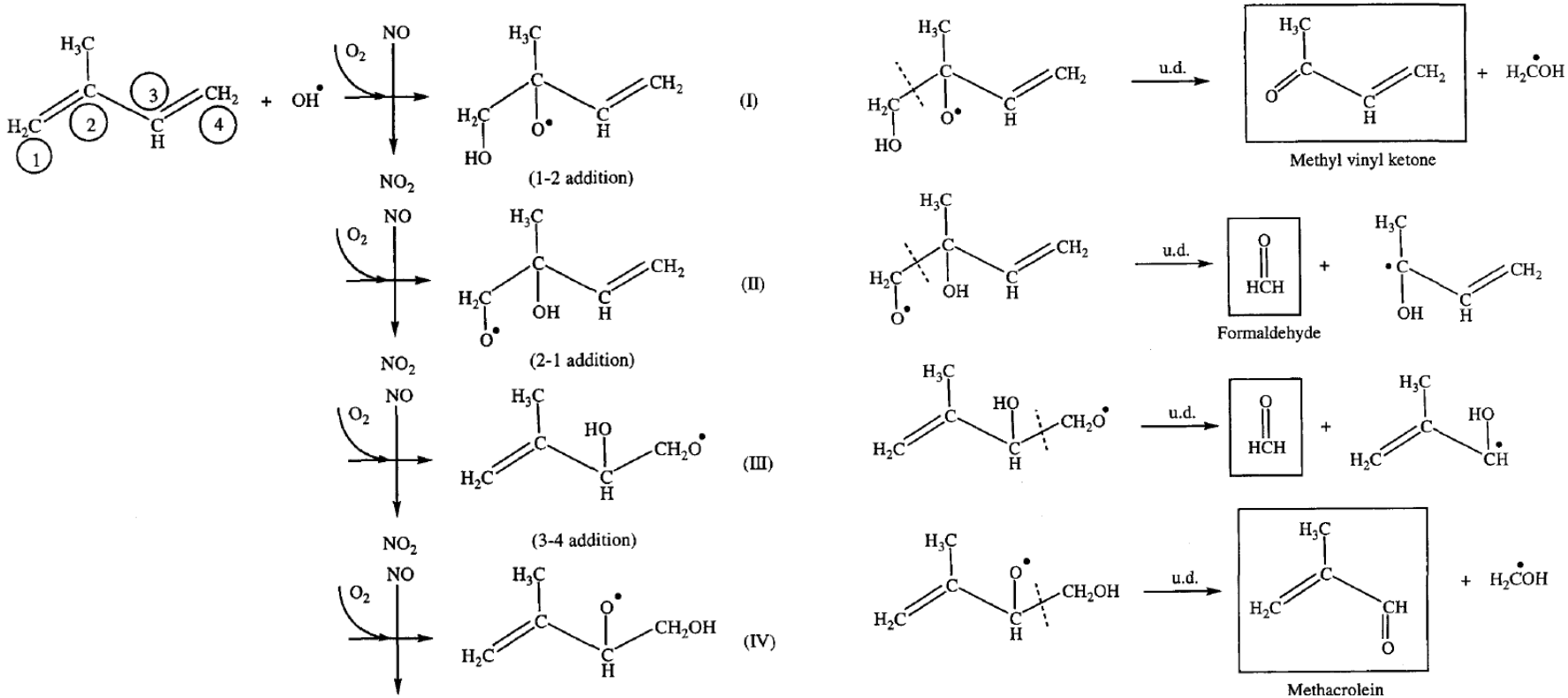
# Alkene + O3


R1
R2
C=C
R3
R4
+ O3
O
O
O
R1
R2
C
C
R3
R4
‡
a
b
O
R1—C—R2
+
[R3R4ĊOO•]‡
O
R3—C—R4
+
[R1R2ĊOO•]‡

# Aromatic Reactions

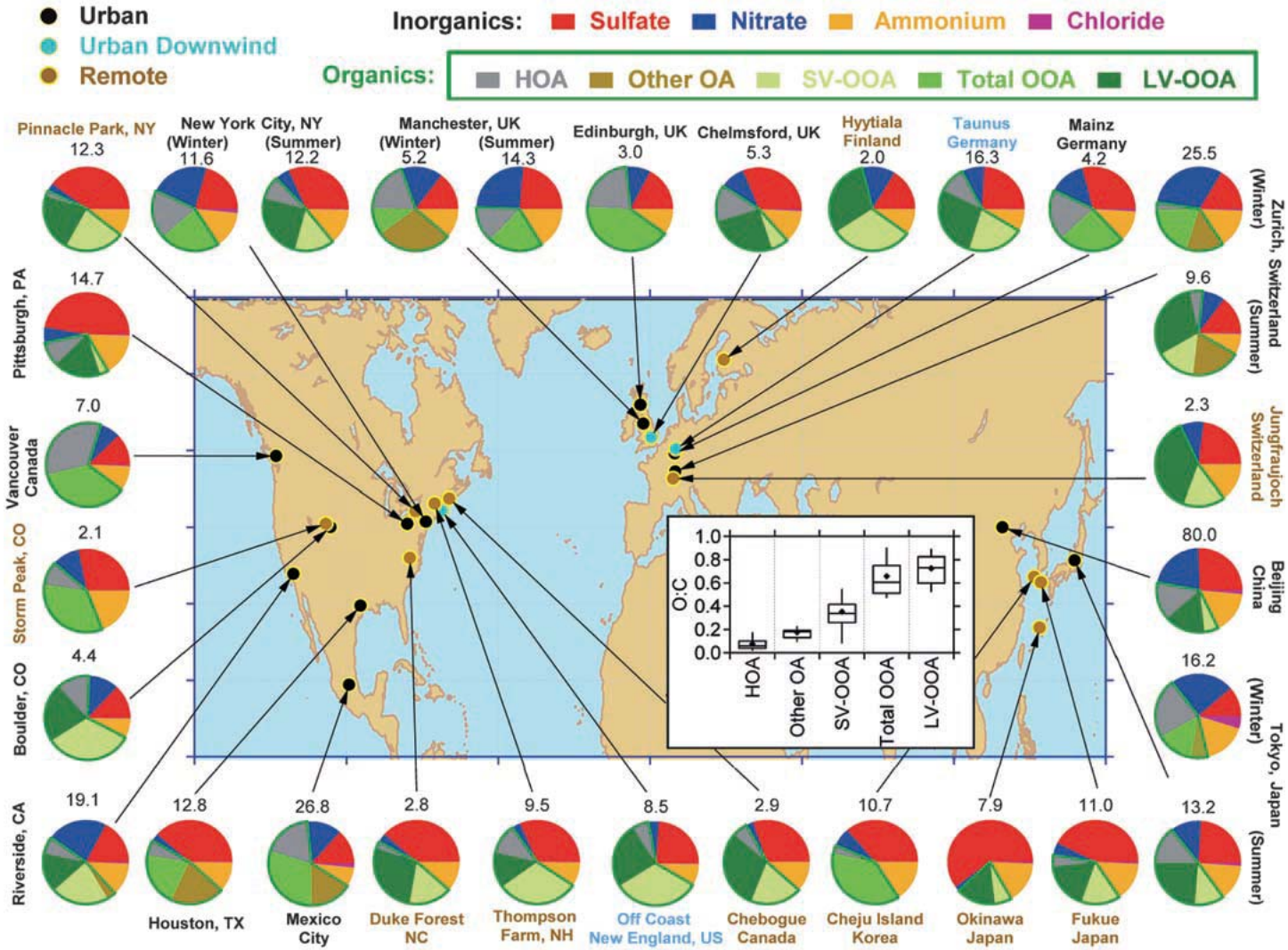


# Isoprene oxidation



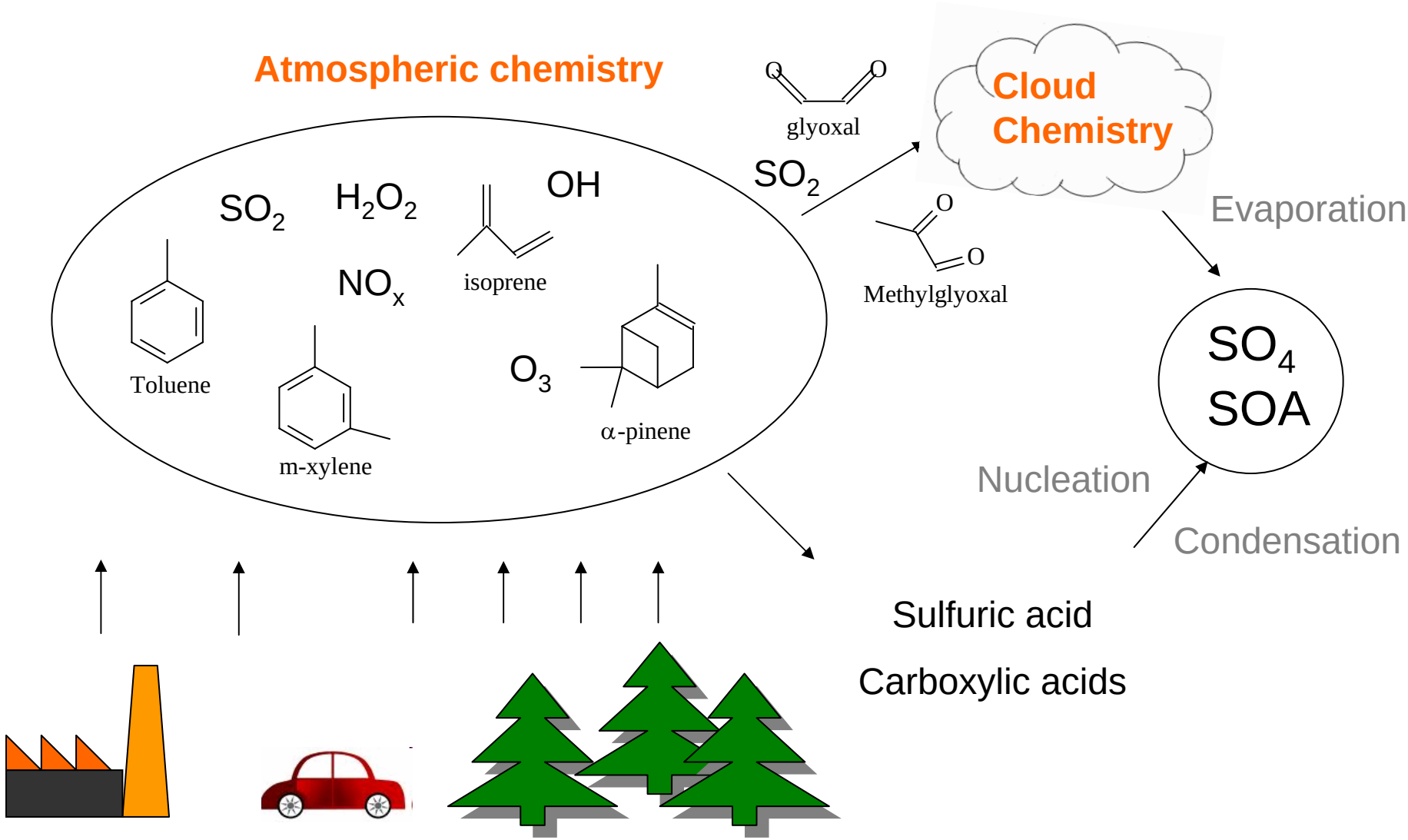
# Formation of secondary organic aerosols

# Motivations (conti…)




Jimenez et al. [2009] *Science*

# Formation of Sulfate and SOA



# Gas-phase production

**Sulfate production:**

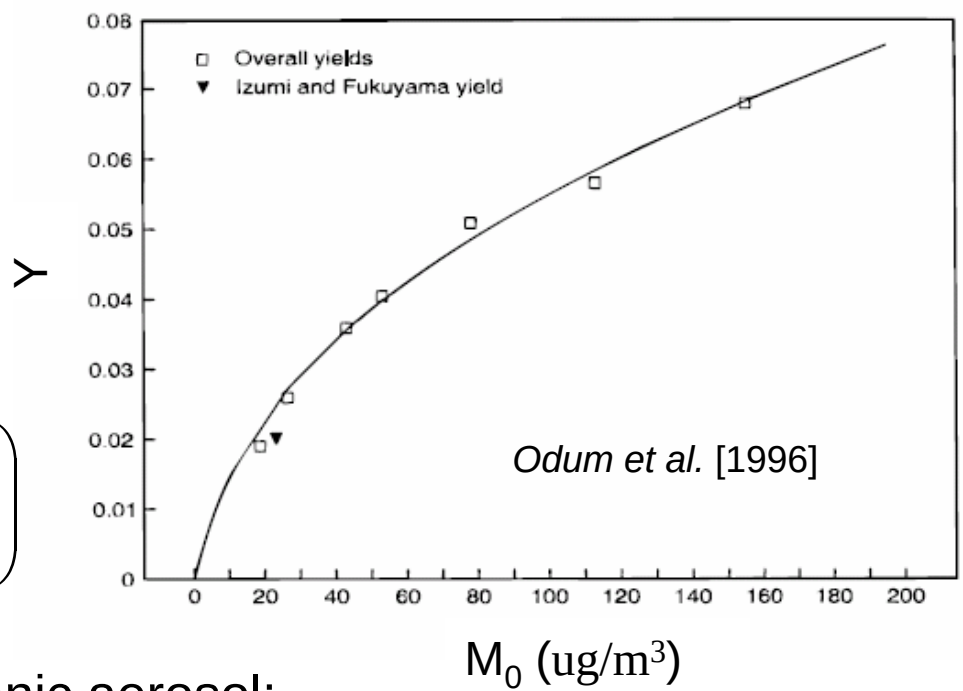
$$SO_2 + OH + M \longrightarrow SO_4 + M$$

**SOA yield is defined as:**

$$Y = \frac{\Delta SOA}{\Delta VOC}$$

**Two-Product model:**

$$Y = \alpha_1 \left( \frac{K_{om,1} M_o}{1 + K_{om,1} M_o} \right) + \alpha_2 \left( \frac{K_{om,2} M_o}{1 + K_{om,2} M_o} \right)$$

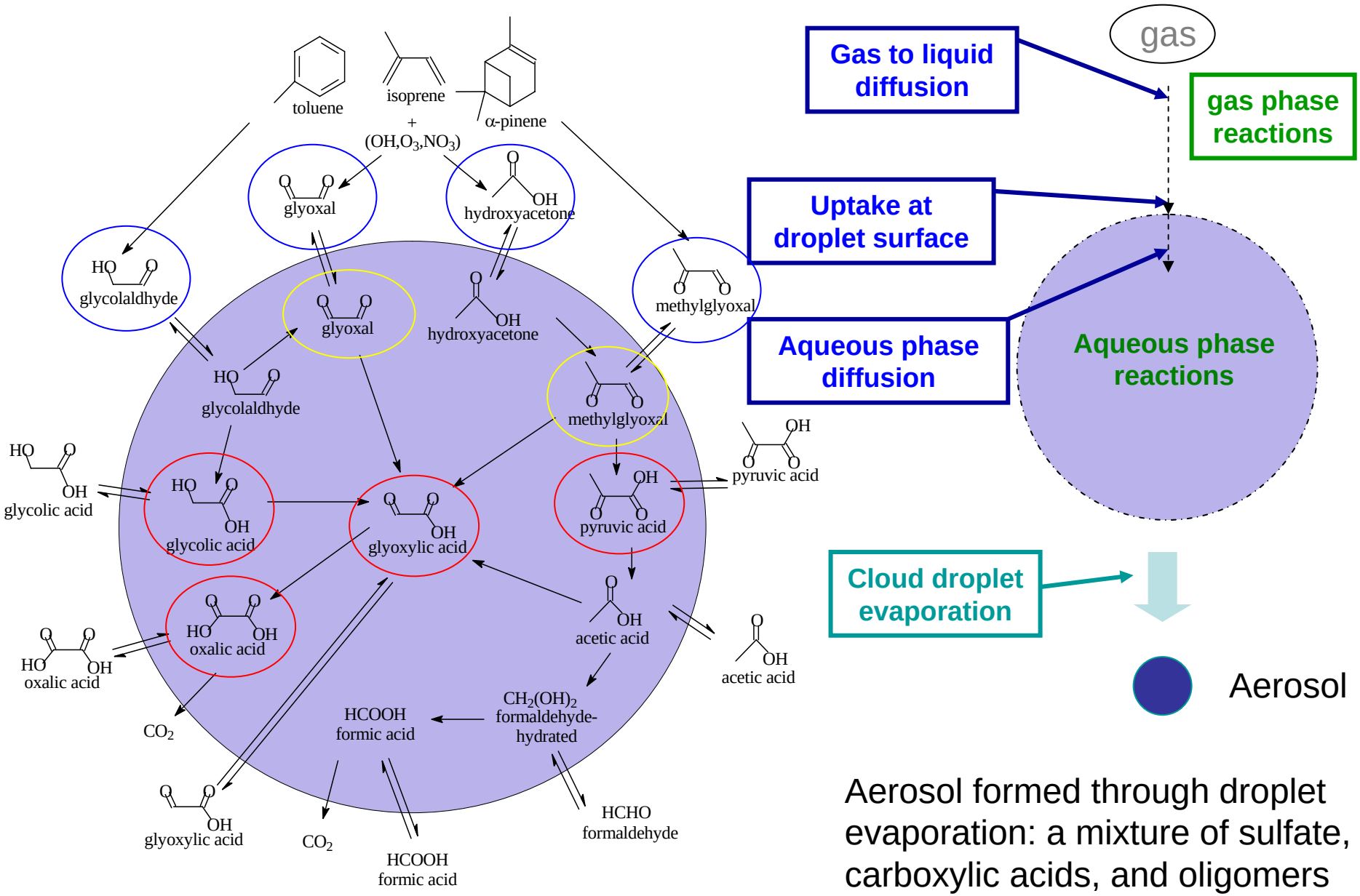



**$M_0$** is the concentration of total organic aerosol;

$\alpha_{1/2}$ is mass based stoichiometric coefficients;

**$K_{om,1/2}$** is equilibrium partition coefficients;

# Mechanism of aqueous-phase SOA production




Aerosol formed through droplet evaporation: a mixture of sulfate, carboxylic acids, and oligomers

# Coupled gas- and aqueous phase chemistry in GFDL coupled chemistry-climate model AM3

- **Gas-phase chemistry** is being updated from MOZART-2 to MOZART-4 chemistry mechanisms [*Horowitz et al.* 2003; *Emmons et al.* 2009]
- **Aqueous chemistry** is based on an optimized mechanism for sulfur chemistry, merged with the updated cloud SOA chemistry [*Jacob* 1986; *Pandis and Seinfeld* 1989; *Ervens et al.* 2004,2008; *Tan et al.* 2009]
- **Coupled mechanism** includes: ~100 gas phase species, ~50 aqueous phase species, and totally ~370 reactions
- **Physical and chemical processes include:**
  - Gas-liquid mass transfer
  - Aqueous-phase ionic equilibrium
  - Cloud hydrogen ion concentrations (or PH value) prediction: based on electroneutrality equation
- **Cloud droplet size:** currently assumed to be10um
- **Cloud droplet lifetime:** model time step (30min) or 10min
- **Could fraction:** coupled chemistry is solved only for the cloudy area.
- **Cloud entrainment:** mixing of outside air into the cloud is neglected.
- **Cloud evaporation:** SOA and sulfate are formed when cloud evaporates

# Global in-cloud production of $SO_4$ and SOA (Tg/yr)

**SO4**

| | |
|---|---|
| Gas-phase production | **22.3** (Tg $SO_4$/yr) |
| Liquid-phase production | **92.6** (Tg $SO_4$/yr) |

**SOA**

| | |
|---|---|
| Gas-phase production | **20 - 30** (Tg/yr) |
| Liquid-phase production | **22 - 30** (Tg/yr) |

# Radiative Flux Perturbation due to IC-SOA (watts/m$^2$)

（with IC-SOA – without）

| **RF change (SW+LW)** | DJF | MAM | JJA | SON | **Average** |
|---|---|---|---|---|---|
| **TOA** | 0.12 | -0.14 | -0.22 | 0.12 | **-0.03** |
| **Surface** | 0.05 | -0.25 | -0.18 | -0.14 | **-0.13** |
| **Atmos. Abs.** | 0.07 | 0.11 | -0.04 | 0.26 | **0.10** |

# Measurements in Beijing City

| | (R) Reference Period (2005-2007) | | (O) Olympic Period (2008) | |
|---|---|---|---|---|
| **PM, BC, $SO_2$ and $NO_2$ ($\mu g/m^3$)** | Mean ± SD | n | Mean ± SD | n |
| $PM_{10}$[e] | 123 ± 55.4 | 245 | 82.5 ± 42.8 | 77 |
| $PM_{2.5}$[f] | 58.5 ± 34.3 | 135 | 58.5 ± 35.8 | 82 |
| BC[g] | 4.6 ± 2.2 | 71 | 3.2 ± 1.1 | 79 |
| $SO_2$[e] | 16 ± 8.6 | 238 | 11 ± 3.5 | 77 |
| $NO_2$[e] | 57 ± 14 | 238 | 28 ± 6.6 | 77 |
| **Ionic species in $PM_{2.5}$ ($\mu g/m^3$)** | Mean ± SD | n | Mean ± SD | n |
| $Na^+$ | 0.43 ± 0.22 | 26 | 0.19 ± 0.16 | 9 |
| $NH_4^+$ | 8.0 ± 3.1 | 31 | 8.4 ± 2.5 | 9 |
| $K^+$ | 1.5 ± 0.59 | 31 | 0.46 ± 0.22 | 9 |
| $Mg^{2+}$ | 0.22 ± 0.10 | 29 | 0.08 ± 0.04 | 8 |
| $Ca^{2+}$ | 1.5 ± 0.74 | 31 | 0.41 ± 0.19 | 6 |
| $Cl^-$ | 0.39 ± 0.22 | 11 | 0.47 | 1 |
| $NO_3^-$ | 1.5 ± 2.2 | 28 | 3.9 ± 1.5 | 9 |
| $SO_4^{2-}$ | 22.3 ± 11.3 | 31 | 13.1 ± 4.8 | 8 |
| Total ions in $PM_{2.5}$ | 35.3 ± 14.9 | 31 | 24.9 ± 10.2 | 9 |

# End

END

# Gas-phase $SO_4$ and SOA production

$SO_4$: $SO_2 + OH \rightarrow SO_4$ **22.3** (Tg $SO_4$/yr)

SOA: two-product model parameterization **30.3** (Tg/yr)

| Precursors | Emissions (Tg/yr) | SOA Production (Tg/yr) | Average Yield (%) | Heald et al. [2008] | Henze et al. [2008] | Lack et al. [2004] |
|---|---|---|---|---|---|---|
| Isoprene | 565.6 | 8.8* | 1.6 | 19.2 | 14.4 | - |
| Terpene | 143.7 | 16.2 | 11.3 | 3.7 | 10.8 | 22.7 |
| Aromatics | 34.3 | 5.2 | 15.1 | 1.4 | 3.5 | - |
| Higher Alkanes | 78.9 | 0.13 | 0.2 | - | - | - |
| Total | 822.5 | 30.3 | | 24.3 | 30.3 | 22.7 |

*NOx dependent SOA production from isoprene, based on *Carlton et al.* [2009]

The SOA production is assumed to be approximately 15% of Terpene emissions in the original AM3 configuration with adjustments on temperature [*Donner et al.,* 2011].