Gaseous Pollutants

- General considerations on gaseous air pollutants
- Oxidizing power of the atmosphere and chemical reactivity
- Gas-phase chemistry of photochemical air pollution
- Emission control strategies
- Chemical kinetic mechanisms for air pollution modeling

Different Phases in the Atmosphere

- Gases
  - Main gases (N_2, O_2)
  - Trace gases (pollutants)
- Liquid water
  - Cloud and fog droplets
  - Rain drops
- Solid water
  - Ice
  - Snow
- Particles
  - Solid
  - Liquid

Types of Chemical Species

- Molecules: for example, NO, NO_2, O_3, etc.; chemically stable species
- Radicals: for example, OH, HO_2, NO_3, etc.; very reactive species, very low concentrations
- Atoms: for example, $O(^3P)$, Hg^0; reactive or stable species, depending on their electronic state
- Excited species: for example, $O(^1D)$; highly reactive species, very low concentrations

$$\underset{\text{molecule}}{\mathrm{NO}} + \underset{\text{radical}}{\mathrm{HO_2}} \Rightarrow \underset{\text{molecule}}{\mathrm{NO_2}} + \underset{\text{radical}}{\mathrm{OH}}$$

Types of Chemical Species

- Pollutants: adverse health and environmental effects
- Precursors: chemical species that produce a pollutant via a chemical reaction
- Oxidants: chemical species that oxidize other species

$$\underset{\text{precursor}}{NO} + \underset{\text{oxidant}}{HO_2} \Rightarrow \underset{\text{pollutant}}{NO_2} + OH$$

Ideal Gas Law

Ideal gas law:

$$P\,V = n\,R\,T$$

P (atm): Atmospheric pressure
V (m^3): Volume of air
T (K): Temperature
$R = 8.31\ \mathrm{J\ K^{-1}\ mole^{-1}} = 8.2 \times 10^{-5}\ \mathrm{atm\ m^3\ K^{-1}\ mole^{-1}}$: Ideal gas law constant
n (moles): number of moles

At $P = 1$ atm and $T = 298$ K (25 ° C): $n / V = 40.9\ \mathrm{moles / m^3}$

$N = 6.02 \times 10^{23}$ molecules per mole ; 1 atm = 2.46×10^{25} molec m^{-3}

Unit Conversions

1 atm = 2.46×10^{25} molecules m^{-3} = 40.9 moles / m^3

At P = 1 atm:
1 ppb = 10^{-9} atm = 2.46×10^{10} molecules cm^{-3} (ppb: parts per billion)

Conversion of $\mu g/m^3$ to ppb
(MW is the molar weight of the chemical species in g/mole):

1 $\mu g/m^3$ = $1O^{-6}$ / MW mole/m^3 = $1O^{-6}$/ (40.9 MW) atm = 10^3 / (40.9 MW) ppb

1 ppb = (40.9 MW) / 10^3 $\mu g/m^3$

For example, for ozone (MW = 48 g/mole): 1 ppb = 2 $\mu g/m^3$

Pollutant Categories

- **NO_x**: NO and NO_2
- NO_y: all nitrogen oxides (except N_2O), i.e., NO, NO_2, NO_3, HNO_3, HNO_2, N_2O_5, organic nitrates
- NO_z: NO_y - NO_x
- **SO_x**: SO_2, SO_3, and H_2SO_4
- **VOC**: volatile organic compounds, i.e., alkanes, alkenes, aldehydes, alcohols, aromatic compounds, etc.
- HC: hydrocarbons (organic compounds with C and H)
- NMHC: non-methane hydrocarbons

Primary and Secondary Pollutants

- Primary pollutants: they are emitted directly into the atmosphere
  - NO and NO_2 (NO_x), SO_2, VOC (for example, HCHO, C_6H_6), etc.

- Secondary pollutants: they are formed in the atmosphere via chemical reactions
  - O_3 (formed from NO_x and VOC), NO_2, HCHO, H_2SO_4, HNO_3, etc.

Main Gaseous Pollutants

- Sulfur dioxide (SO_2): Regulated air pollutant (respiratory health effects) and precursor of secondary particulate matter (PM) and sulfuric acid (contributor to acid rain)
- Carbon monoxide (CO): Regulated air pollutant (anoxia) and precursor of ozone
- Ozone (O_3): Regulated secondary pollutant (respiratory health effects)
- Nitrogen oxides (NO and NO_2): Precursors of secondary PM, ozone, and nitric acid (contributor to acid rain), precursor of nitrogenous species contributing to eutrophication, NO_2 is a regulated air pollutant (respiratory health effects)
- Volatile organic compounds (VOC): Precursors of secondary PM and ozone, some VOC are carcinogenic
- Semi-volatile organic compounds (SVOC): Precursors of secondary PM
- Ammonia (NH_3): Precursor of secondary PM

Urban Air Pollution

Urban air pollution is due to gaseous and particulate (aerosols) air pollutants.

Air pollution has adverse effects on health, atmospheric visibility, vegetation, and materials.

Currently, emissions of SO_2 and CO from vehicles and industries are regulated in North America and Europe and the corresponding ambient concentrations have decreased considerably over the past decades.

Today, the focus of urban air quality policies for gaseous air pollutants concerns mostly ozone (O_3) and nitrogen dioxide (NO_2).

Photochemical "Smog"

"**Smog**": Smoke + fog

Pollutants + solar radiation => **photochemical** pollution

Photochemical smog:
- **Gaseous pollutants (ozone, nitrogen dioxide, formaldehyde, acroleine …)**
- Particles

Background Pollution

Some pollutants have a lifetime of several days and can, therefore, be transported over long distances by the wind and thereby contribute to continental and regional background pollution.

Urban pollution results not only from pollutant emissions from local sources but also from the long-range transport of pollutants from distant sources.

Importance of Atmospheric Ozone

- Radiative properties in the stratosphere: Problem of the destruction of the stratospheric ozone layer
- Air pollutant in the lower atmosphere (troposphere): adverse health effects (pulmonary irritant) and damage to vegetation
- Greenhouse gas
- Precursor of the hydroxyl radical, OH, which is the main oxidant in the atmosphere

Daytime Chemistry and Nighttime Chemistry

- Daytime chemistry:
  - Photolysis => atoms and radicals => high reactivity of the atmosphere

- Nighttime chemistry
  - No photolysis => few radicals => low reactivity of the atmosphere

Stratosphere and Troposphere

- Stratosphere :
  - O_2 and O_3 absorb ultraviolet solar radiation ($\lambda < 290$ nm)
  - Source of atomic oxygen to form O_3:

    $O_2 + h\nu \Rightarrow O + O \qquad \lambda < 242$ nm

- Troposphere
  - Solar radiation, which is effective for photolysis, is in the range:

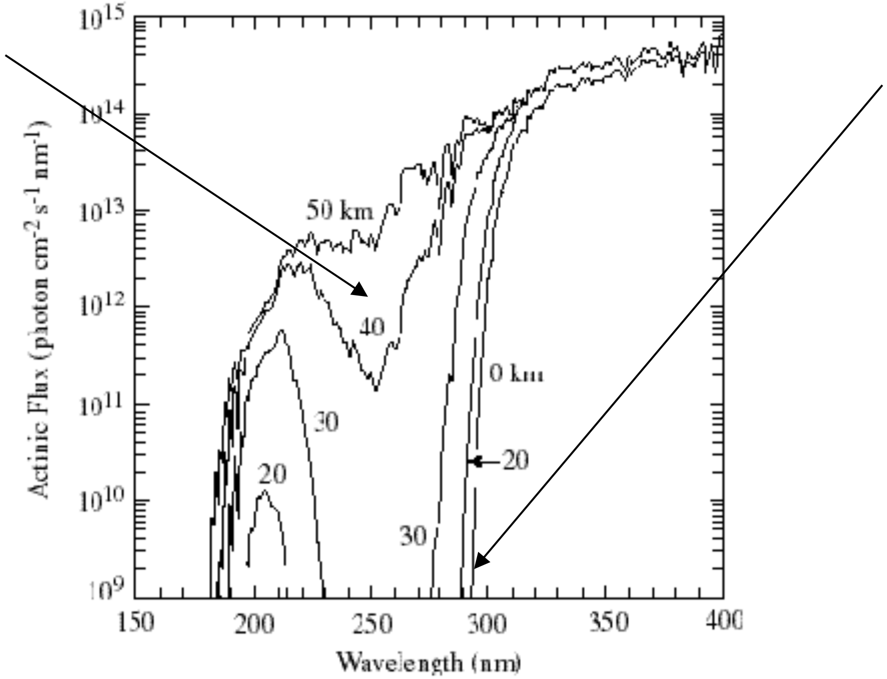
    290 nm $< \lambda <$ 730 nm; i.e., there is no O_2 photolysis.
  - Source of atomic oxygen to form O_3:

    $NO_2 + h\nu \Rightarrow NO + O \qquad 300 < \lambda < 420$ nm

Stratosphere and Troposphere

Stratosphere

Troposphere
(< 15 km)



Actinic flux as a function of wavelength
at different altitudes in the atmosphere

Source: DeMore et al., 1997, Publication 97-4, Jet Propulsion Laboratory, Pasadena, California.

Oxidizing Power of the Atmosphere

- Production of OH
  - Ozone photolysis leads to OH production:

$$O_3 + h\nu\ (\lambda < 310\ \text{nm}) \Rightarrow O_2 + O(^1D)$$

The excited oxygen atom becomes stable by reaction with a molecule:

$$O(^1D) + M \Rightarrow O(^3P) + M$$

$$O(^1D) + H_2O \Rightarrow 2\ OH$$

Oxidizing Power of the Atmosphere

- The cleansing of the atmosphere occurs mostly via the oxidation of organic and inorganic chemical species
  - Organic species => CO_2 and H_2O
  - Inorganic species => acids, nitrates, sulfates…

- The three main oxidants are: OH, O_3, and NO_3
  - OH: mostly during daytime (product of photolysis)
  - O_3: both during daytime and nighttime
  - NO_3: mostly at night (photolyzed during the day)

Chemical Lifetime of a Chemical Species

- The lifetime indicates the chemical stability of the chemical species
- For example, oxidation reaction of chemical species X_i by OH:

$X_i + OH \Rightarrow \ldots$, with $k_{OH}(T)$ as the kinetic constant

Destruction term: $-k_{OH}\,[OH]\,[X_i]$, which leads to a characteristic time:

$$t_{l,i} = 1 / (k_{OH}\,[OH])$$

$t_{l,i}$ is also called the chemical lifetime or residence time.

It should not be confused with the half-life, which corresponds to the time at which half of the reactant, X_i, has been consumed:

$$t_{1/2} = \ln(2) / (k_{OH}\,[OH]) = 0.7\ t_{l,i}$$

Lifetimes of some VOC in the Lower Troposphere

Chemical species	Photolysis[a]	OH	NO_3	O_3
NO_2	-	30 h	-	-
SO_2	-	12 d	-	-
CO	-	48 d	-	-
Methane	-	5 a	> 300 a	-
Propane	-	11 d	> 4 a	-
n-Butane	-	5 d	7 a	-
Hexane	-	2 d	3 a	-
Octane	-	36 h	20 mo	-
Ethylene	-	33 h	19 mo	7 d
Propylene	-	11 h	12 d	28 h
trans-2-Butene	-	4 h	7 h	90 min
1,3-Butadiene	-	4 h	28 h	44 h
1-Hexene	-	8 h	-	25 h
trans-3-Hexene	-	-	-	100 min
trans-4-Octene	-	4 h	-	2 h
Benzene	-	8 d	11 a	-
Toluene	-	2 d	5 a	-
o-Xylene	-	20 h	9 mo	-
Formaldehyde	18 h	33 h	7 mo	-
Acetaldehyde	9 d	18 h	45 d	-
Isoprene	-	3 h	4 h	22 h
MBO	-	4 h	10 d	31 h
α-Pinene	-	5 h	27 min	3 h
Δ^3-Carene	-	3 h	18 min	8 h
Humulene	-	1 h	5 min	1 min
Longifolene	-	6 h	4 h	> 23 d

Concentrations: $[OH] = 2 \times 10^6$ cm^{-3} over 12 h per day (daytime); $[NO_3] = 2 \times 10^8$ cm^{-3} over 12 h per day (nighttime); $[O_3]$ = 40 ppb over 24 h per day. Photolysis for the spring equinox in Paris calculated over 24 h.

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Propane	-	11 d	> 4 a	-
n-Butane	-	5 d	7 a	-
Hexane	-	2 d	3 a	-
Octane	-	36 h	20 mo	-
Ethylene	-	33 h	19 mo	7 d
Propylene	-	11 h	12 d	28 h
trans-2-Butene	-	4 h	7 h	90 min
1,3-Butadiene	-	4 h	28 h	44 h
1-Hexene	-	8 h	-	25 h
trans-3-Hexene	-	-	-	100 min
trans-4-Octene	-	4 h	-	2 h
Benzene	-	8 d	11 a	-
Toluene	-	2 d	5 a	-
o-Xylene	-	20 h	9 mo	-
Formaldehyde	18 h	33 h	7 mo	-
Acetaldehyde	9 d	18 h	45 d	
Isoprene	-	3 h	4 h	22 h
MBO	-	4 h	10 d	31 h
α-Pinene	-	5 h	27 min	3 h
Δ^3-Carene	-	3 h	18 min	8 h
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Alkanes

Aldehydes

Anthropogenic alkenes

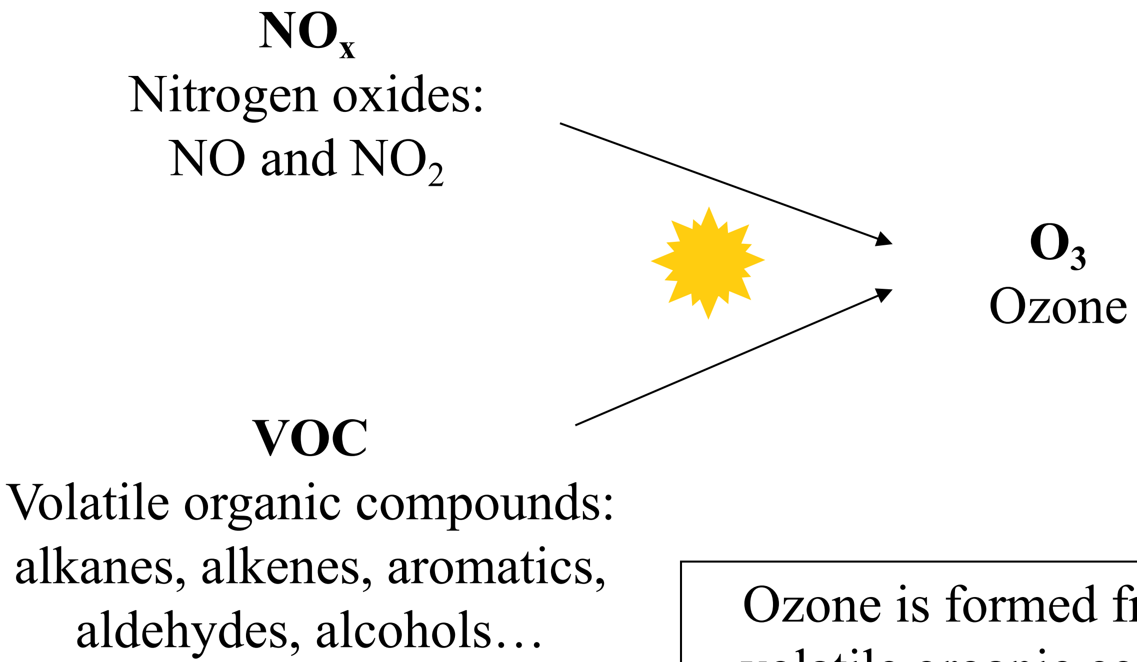
Biogenic alkenes

Discovery of “Photochemical Smog”

- Arie Haagen-Smit, a professor of biochemistry at the California Institute of Technology (Caltech), proposed and demonstrated in 1952 that air pollution in Los Angeles was due to reactions among nitrogen oxides (NO_x) and volatile organic compounds (VOC) in the presence of solar radiation.

Haagen-Smit, A.J. Chemistry and Physiology of Los Angeles Smog; *Ind. Eng. Chem*. **44**, 1342-1346, 1952.

Photochemical Smog: Ozone Formation



NO_x
Nitrogen oxides:
NO and NO_2

VOC
Volatile organic compounds:
alkanes, alkenes, aromatics,
aldehydes, alcohols…

O_3
Ozone

Ozone is formed from nitrogen oxides and volatile organic compounds reacting in the presence of sunlight: It is a non-linear system

Oxidants of Photochemical Smog

- Hydroxyl radical: OH

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

$$O(^1D) + H_2O \Rightarrow 2\,OH$$

$$H_2O_2 + h\nu \Rightarrow 2\,OH$$

$$HNO_2 + h\nu \Rightarrow NO + OH$$

- Ozone: O_3

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

$$O + O_2 \Rightarrow O_3$$

- Nitrate radical: NO_3

$$NO_2 + O_3 \Rightarrow NO_3 + O_2$$

The Photostationary State

Ozone formation:

$NO_2 + hv$ => $NO + O$

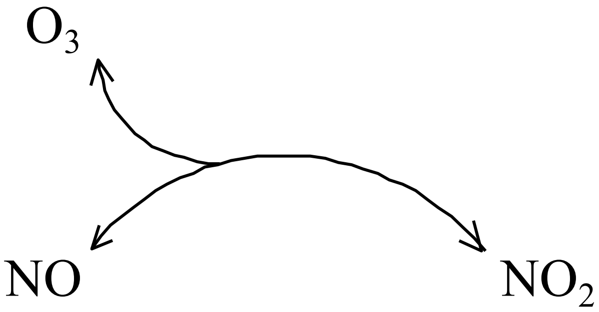
$O + O_2$ => O_3

Ozone destruction:

$NO + O_3$ => $NO_2 + O_2$

The net chemical budget is zero

This is also known as the Leighton cycle.



The Photostationary State

$NO_2 + h\nu \Rightarrow NO + O \qquad k_1$

$O + O_2 \Rightarrow O_3 \qquad k_2$

$NO + O_3 \Rightarrow NO_2 + O_2 \qquad k_3$

Philip A. Leighton, Professor of chemistry at Stanford University, introduced the concept of a photostationry state among these three reactions: at equilibrium, all reaction rates are equal. This is the photostationary state of Leighton

$$k_1\,[NO_2] = k_2[O]\,[O_2] = k_3\,[NO]\,[O_3]$$

The Photostationary State of Leighton

$NO_2 + hv$ => $NO + O$ k_1

$O + O_2$ => O_3 k_2

$NO + O_3$ => $NO_2 + O_2$ k_3

At equilibrium (photostationary state), all reaction rates are equal:

$$k_1\,[NO_2] = k_2[O]\,[O_2] = k_3\,[NO]\,[O_3]$$

thus: $[O_3] = (k_1\,[NO_2]) / (k_3\,[NO])$

The ozone concentration produced by this reaction cycle is low.

Chain of Oxidation of Carbon Monoxide CO

Propragation reactions

$$\begin{array}{lcl} CO + OH & \Rightarrow & CO_2 + H \\ H + O_2 + M & \Rightarrow & HO_2 + M \\ HO_2 + NO & \Rightarrow & OH + NO_2 \\ \hline CO + NO + O_2 & \Rightarrow & CO_2 + NO_2 \end{array}$$

Ozone formation

$$\begin{array}{lcl} NO_2 + h\nu & \Rightarrow & NO + O \\ O + O_2 & \Rightarrow & O_3 \\ \hline NO_2 + O_2 & \Rightarrow & NO + O_3 \end{array}$$

Net budget

$$CO + 2\,O_2 \overset{NO_x}{\Rightarrow} CO_2 + O_3$$

Thus, the oxidation of one molecule of carbon monoxide leads to **one** additional ozone molecule

Chain of Oxidation of Carbon Monoxide (CO)

Propagation reactions

Hydroperoxyl radical

$$\begin{aligned} CO + OH &\Rightarrow CO_2 + H \\ H + O_2 + M &\Rightarrow HO_2 + M \\ HO_2 + NO &\Rightarrow OH + NO_2 \\ \hline CO + NO + O_2 &\Rightarrow CO_2 + NO_2 \end{aligned}$$

Ozone formation

$$\begin{aligned} NO_2 + h\nu &\Rightarrow NO + O \\ O + O_2 &\Rightarrow O_3 \\ \hline NO_2 + O_2 &\Rightarrow NO + O_3 \end{aligned}$$

Net budget

$$CO + 2\,O_2 \overset{NO_x}{\Rightarrow} CO_2 + O_3$$

Thus, the oxidation of one molecule of carbon monoxide leads to **one** additional ozone molecule.

Ozone Formation
Perturbation of the Photostationary Cycle

Ozone formation

$$NO_2 + h\nu \Rightarrow NO + O \quad (1)$$
$$O + O_2 \Rightarrow O_3 \quad (2)$$

Oxidation of NO to NO_2 with destruction of O_3

$$O_3 + NO \Rightarrow O_2 + NO_2 \quad (3)$$

Oxidation of NO to NO_2 without destruction of O_3

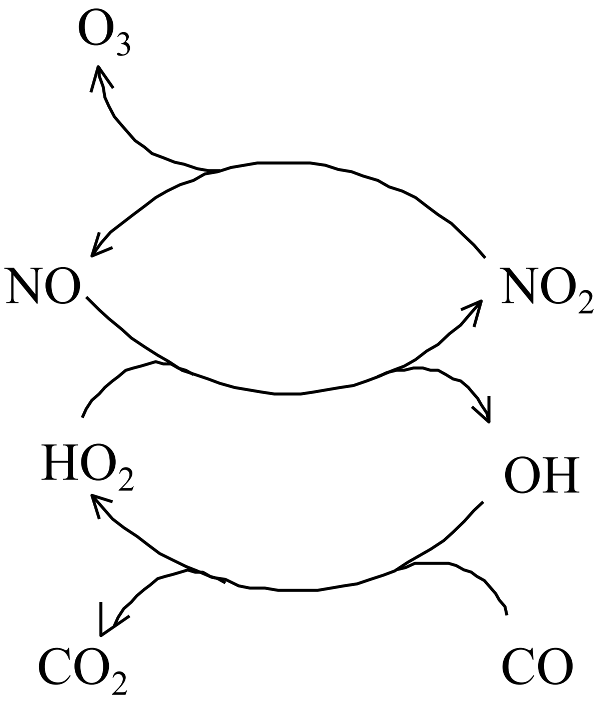
$$HO_2 + NO \Rightarrow OH + NO_2 \quad (4)$$

Budget of reactions (1), (2) and (4) :

$$HO_2 + O_2 \Rightarrow OH + O_3$$

Photochemical Smog

The oxidation of CO perturbs the photostationary cycle by converting NO to NO_2 without O_3 destruction and leads to ozone formation



The oxidation of volatile organic compounds (VOC) leads to ozone formation in the same manner.

Volatile Organic Compounds (VOC)

The main categories of VOC are the following:

- Alkanes: hydrocarbons (C and H) with single C-C bonds
- Alkenes: hydrocarbons (C and H) with one or more double C=C bonds
- Aromatic compounds: a phenyl ring
- Aldehydes: a carbonyl group (-HC=O)
- Ketones: An oxo group (C=O)
- Alcohols: C-OH
- Ethers: C-O-C

Oxidation of VOC

The oxidation pathways for VOC are the following:

- Photolysis (mostly for aldehydes)
- Reaction with OH
- Reaction with NO_3
- Reaction with O_3 (for alkenes only)
- Reaction with $O(^3P)$ (negligible)

Oxidation of Formaldehyde (HCHO)

$$\begin{array}{lll}
\mathrm{HCHO} + hv & \Rightarrow & \mathrm{H} + \mathrm{HCO} \\
\mathrm{H} + \mathrm{O_2} & \Rightarrow & \mathrm{HO_2} \\
\mathrm{HCO} + \mathrm{O_2} & \Rightarrow & \mathrm{HO_2} + \mathrm{CO} \\
\hline
\mathrm{HCHO} + hv + 2\,\mathrm{O_2} & \Rightarrow & 2\,\mathrm{HO_2} + \mathrm{CO}
\end{array}$$

$$\mathrm{HCHO} + hv \quad \Rightarrow \quad \mathrm{H_2} + \mathrm{CO}$$

$$\begin{array}{lll}
\mathrm{HCHO} + \mathrm{OH} & \Rightarrow & \mathrm{HCO} + \mathrm{H_2O} \\
\mathrm{HCO} + \mathrm{O_2} & \Rightarrow & \mathrm{HO_2} + \mathrm{CO} \\
\hline
\mathrm{HCHO} + \mathrm{OH} + \mathrm{O_2} & \Rightarrow & \mathrm{HO_2} + \mathrm{CO} + \mathrm{H_2O}
\end{array}$$

Oxidation of Formaldehyde (HCHO)

Hydroperoxyl radical

$HCHO + h\nu \Rightarrow H + HCO$

$H + O_2 \Rightarrow HO_2$

$HCO + O_2 \Rightarrow HO_2 + CO$

$HCHO + h\nu + 2\,O_2 \Rightarrow 2\,HO_2 + CO$

$HCHO + h\nu \Rightarrow H_2 + CO$

$HCHO + OH \Rightarrow HCO + H_2O$

$HCO + O_2 \Rightarrow HO_2 + CO$

$HCHO + OH + O_2 \Rightarrow HO_2 + CO + H_2O$

Oxidation of Formaldehyde (HCHO)

On average:

$$\begin{array}{ll}
\mathrm{HCHO} + (hv,\ \mathrm{OH}) + \mathrm{O_2} & => \mathrm{HO_2} + \mathrm{CO} + (1/2\ \mathrm{H_2}, \mathrm{H_2O}) \\
\mathrm{NO} + \mathrm{HO_2} & => \mathrm{NO_2} + \mathrm{OH} \\
\mathrm{NO_2} + hv & \overset{(+\mathrm{O2})}{=>} \mathrm{NO} + \mathrm{O_3} \\
\hline
\mathrm{HCHO} + (hv,\ \mathrm{OH}) + 2\ \mathrm{O_2} & => \mathrm{O_3} + \mathrm{CO} + (1/2\ \mathrm{H_2}, \mathrm{H_2O}) + \mathrm{OH}
\end{array}$$

Therefore, the oxidation of one molecule of formaldehyde leads to **two** additional molecules of ozone.

Oxidation of Acetaldehyde (CH_3CHO)

Methylperoxyl radical

$CH_3CHO + hv \Rightarrow CH_3 + HCO$
$CH_3 + O_2 \Rightarrow CH_3O_2$
$HCO + O_2 \Rightarrow HO_2 + CO$

$CH_3CHO + hv \Rightarrow CH_3O_2 + HO_2 + CO$

$CH_3CHO + hv \Rightarrow CH_4 + CO$

$CH_3CHO + OH \Rightarrow CH_3CO + H_2O$
$CH_3CO + O_2 \Rightarrow CH_3C(O)O_2$
$CH_3C(O)O_2 + NO_2 <=> CH_3C(O)O_2NO_2$ [peroxyacetyl nitrate or PAN]
$CH_3C(O)O_2 + NO \Rightarrow CH_3C(O)O + NO_2$
$CH_3C(O)O + O_2 \Rightarrow CH_3O_2 + CO_2$

Oxidation of Methane (CH_4)

$CH_4 + OH \Rightarrow CH_3 + H_2O$

Methylperoxyl radical

$CH_3 + O_2 \Rightarrow CH_3O_2$

$CH_3O_2 + NO \Rightarrow CH_3O + NO_2$

$CH_3O + O_2 \Rightarrow HCHO + HO_2$

$CH_3O_2 + NO_2 \Leftrightarrow CH_3ONO_3$

$NO + HO_2 \Rightarrow NO_2 + OH$

$2\ NO_2 + hv \overset{(+2\ O2)}{\Rightarrow} 2\ NO + 2\ O_3$

$CH_4 + 4\ O_2 \Rightarrow 2\ O_3 + HCHO + H_2O$

Therefore, the oxidation of one molecule of methane leads to **four** additional molecules of ozone; however, it is slow.

Oxidation of Alkanes by OH

$$\mathrm{RH + OH \Rightarrow R + H_2O} \qquad \mathrm{(for\ CH_4,\ R = CH_3)}$$

$$\mathrm{R + O_2 \Rightarrow RO_2}$$

$$\mathrm{RO_2 + NO \Rightarrow RO + NO_2}$$

$$\mathrm{RO + O_2 \Rightarrow R'CHO + HO_2} \qquad \mathrm{(R' = R - 1\ CH_2)}$$

$$\mathrm{NO + HO_2 \Rightarrow NO_2 + OH}$$

$$\mathrm{2\ NO_2} + hv \overset{\mathrm{(+2\ O2)}}{\Rightarrow} \mathrm{2\ NO + 2\ O_3}$$

$$\mathrm{RH + 4\ O_2 \Rightarrow 2\ O_3 + R'CHO + H_2O}$$

Therefore, the oxidation of one alkane molecule leads to two ozone molecules and one aldehyde, which will lead to at least two ozone molecules.

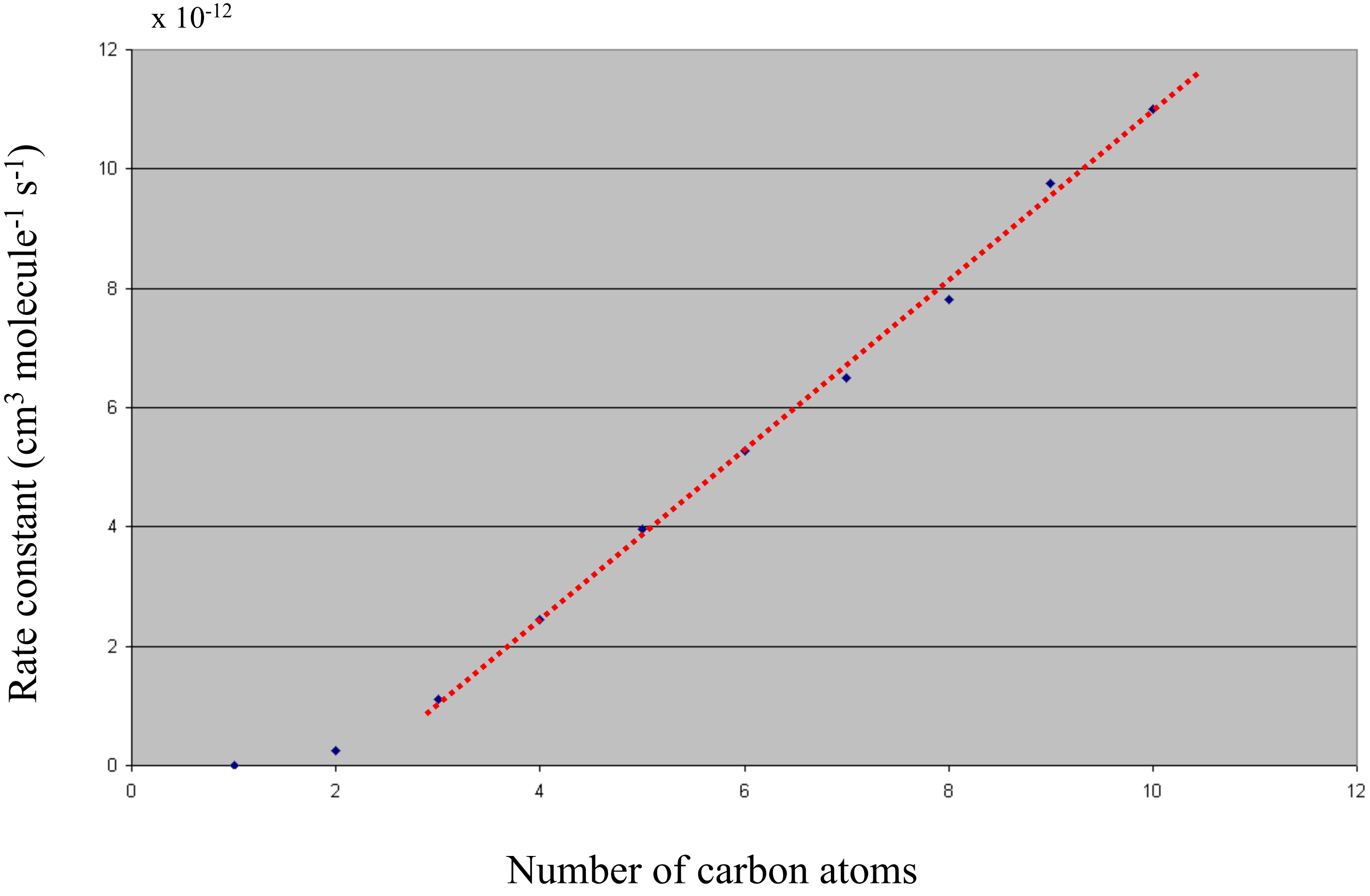
Oxidation of Alkanes by OH

Alkylperoxyl radical

$$
\begin{array}{lll}
RH + OH & => & R + H_2O \\
R + O_2 & => & \boxed{RO_2} \\
RO_2 + NO & => & RO + NO_2 \\
RO + O_2 & => & R'CHO + HO_2 \quad (R' = R - 1\ CH_2) \\
NO + HO_2 & => & NO_2 + OH \\
2\ NO_2 + hv & \overset{(+2\ O2)}{=>} & 2\ NO + 2\ O_3 \\
\hline
RH + 4\ O_2 & => & 2\ O_3 + R'CHO + H_2O
\end{array}
$$

Therefore, the oxidation of one alkane molecule leads to two ozone molecules and one aldehyde, which will lead to at least two ozone molecules.

Kinetics of Oxidation of Alkanes by OH



The reaction rate increases with the number of carbon atoms of the alkane molecule.

Alkane Oxidation by NO_3

The first step differs from that of oxidation by OH:

$$RH + OH \Rightarrow R + H_2O$$

$$RH + NO_3 \Rightarrow R + HNO_3$$

The oxidation of alkanes by NO_3 is very slow (i.e., negligible).

Alkene Oxidation by OH

The oxidation path differs from that of alkanes because, instead of the abstraction of a hydrogen atom, the OH radical is added to the double bond.

Example of ethylene (ethene):

$$H_2C{=}CH_2 + OH \quad => \quad HOCH_2CH_2$$

$$HOCH_2CH_2 + O_2 \quad => HOCH_2CH_2O_2$$

$$HOCH_2CH_2O_2 + NO \quad => HOCH_2CH_2O + NO_2$$

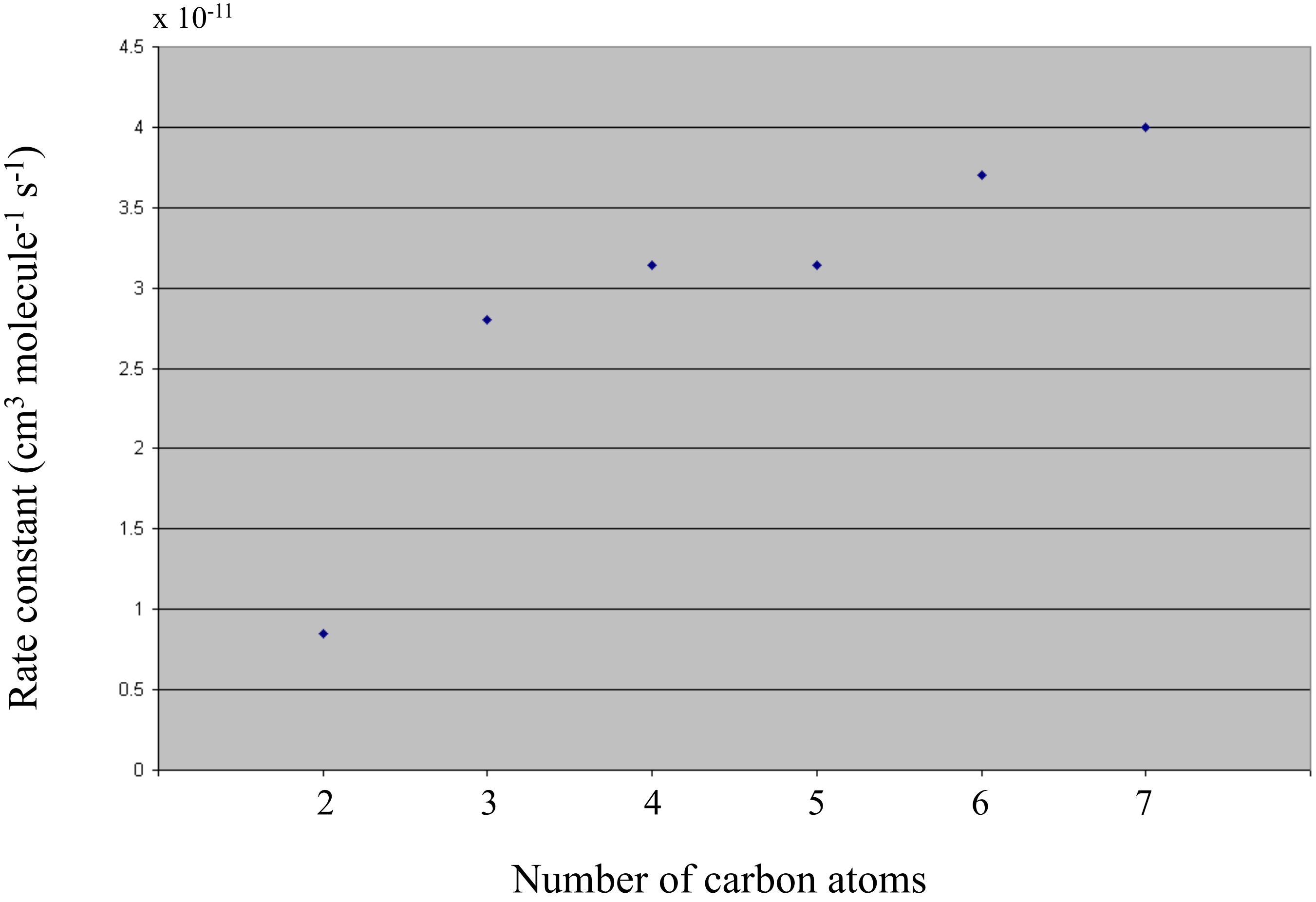
$$HOCH_2CH_2O \quad \overset{(72\ \%)}{=>} 2\ HCHO + HO_2$$

$$HOCH_2CH_2O \quad \overset{(28\ \%)}{=>} HOCH_2CHO + HO_2$$

$$C_2H_4 + OH + 2\ NO => 1.4\ HCHO + 0.3\ HOCH_2CHO + OH + 2\ NO_2$$

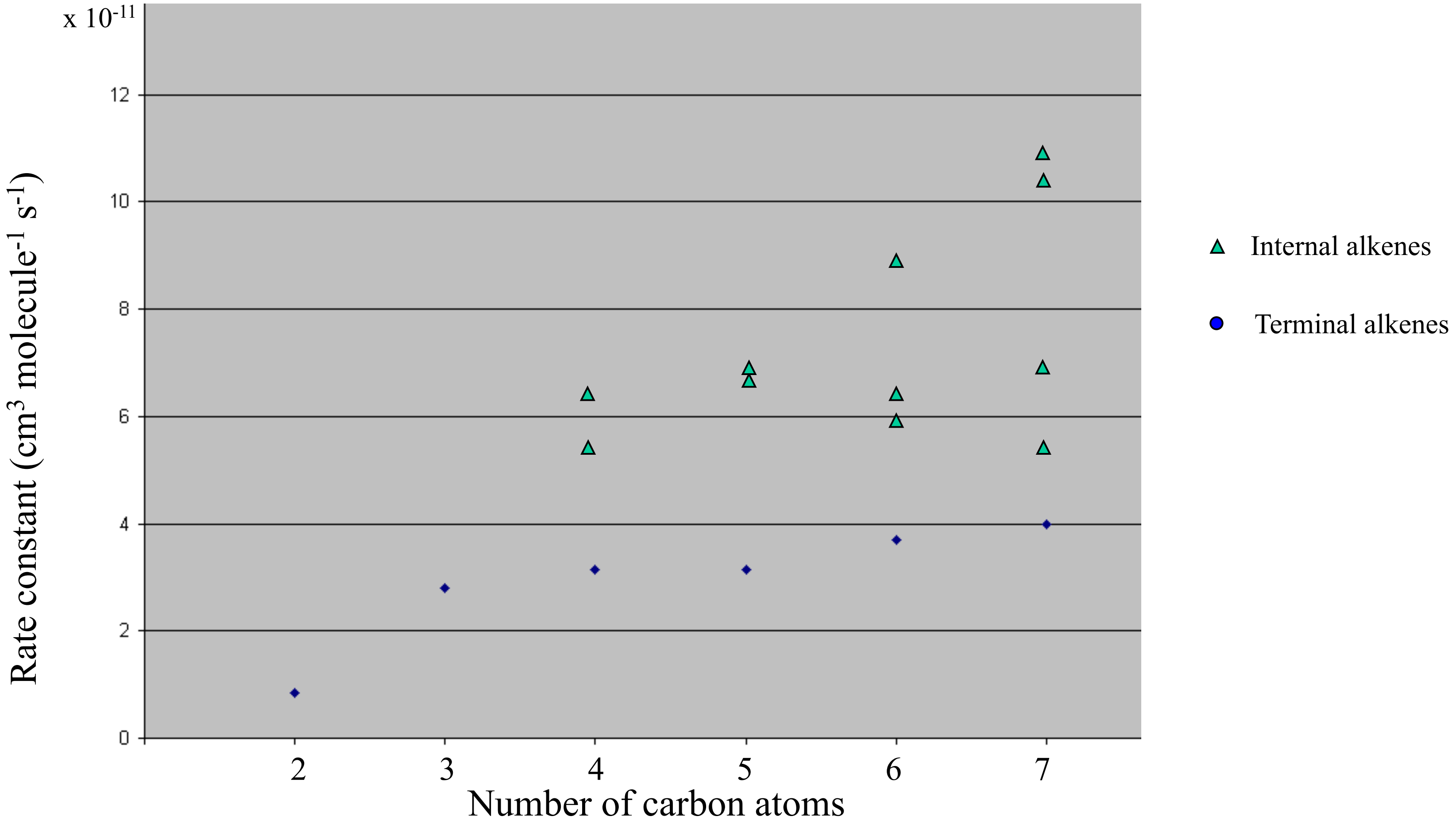
Kinetics of Terminal Alkene Oxidation by OH

A terminal alkene has the double-bond at the end of the molecule.



Kinetics of Terminal and Internal Alkene Oxidation by OH

Oxidation is faster if the double-bond is not at the end of the molecule (internal).



Alkene Oxidation by NO_3

The oxidation path differs from that of alkanes because, instead of the abstraction of a hydrogen atom, the NO_3 radical is added to the double bond.

$$R_1R_2C{=}CR_3R_4 + NO_3 \Rightarrow R_1R_2C(ONO_2)\text{-}CR_3R_4$$

$$R_1R_2C(ONO_2)\text{-}CR_3R_4 + O_2 \Rightarrow R_1R_2C(ONO_2)\text{-}C(O_2)R_3R_4$$

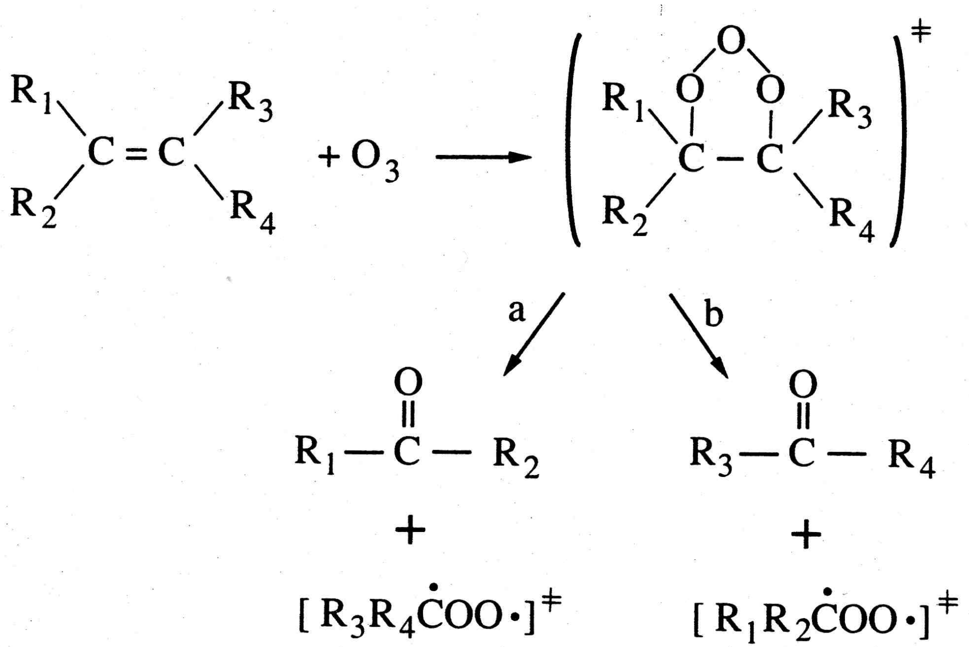
$$R_1R_2C(ONO_2)\text{-}C(O_2)R_3R_4 + HO_2 \Rightarrow \text{organic nitrate, ketones}$$

$$R_1R_2C(ONO_2)\text{-}C(O_2)R_3R_4 + CH_3O_2 \Rightarrow \text{organic nitrate, ketones}$$

Note that the organic peroxyl radical does not react with NO to form NO_2, because NO concentrations are negligible when NO_3 is present (O_3 reacts much faster with NO than with NO_2); therefore, oxidation by NO_3 does not lead to O_3 formation.

Alkene Oxidation by O_3

Oxidation by O_3 is specific to alkenes:



Ozonide

Carbonyl compounds

Criegee biradicals

R_1R_2COO => stable products + radicals => formation of O_3

Oxidation of Aromatic Compounds by OH

The oxidation of aromatic compounds differs from that of alkanes because the abstraction of a hydrogen atom by OH (to form H_2O) is a minor oxidation path (< 10 %; formation of benzaldehyde in the case of toluene).

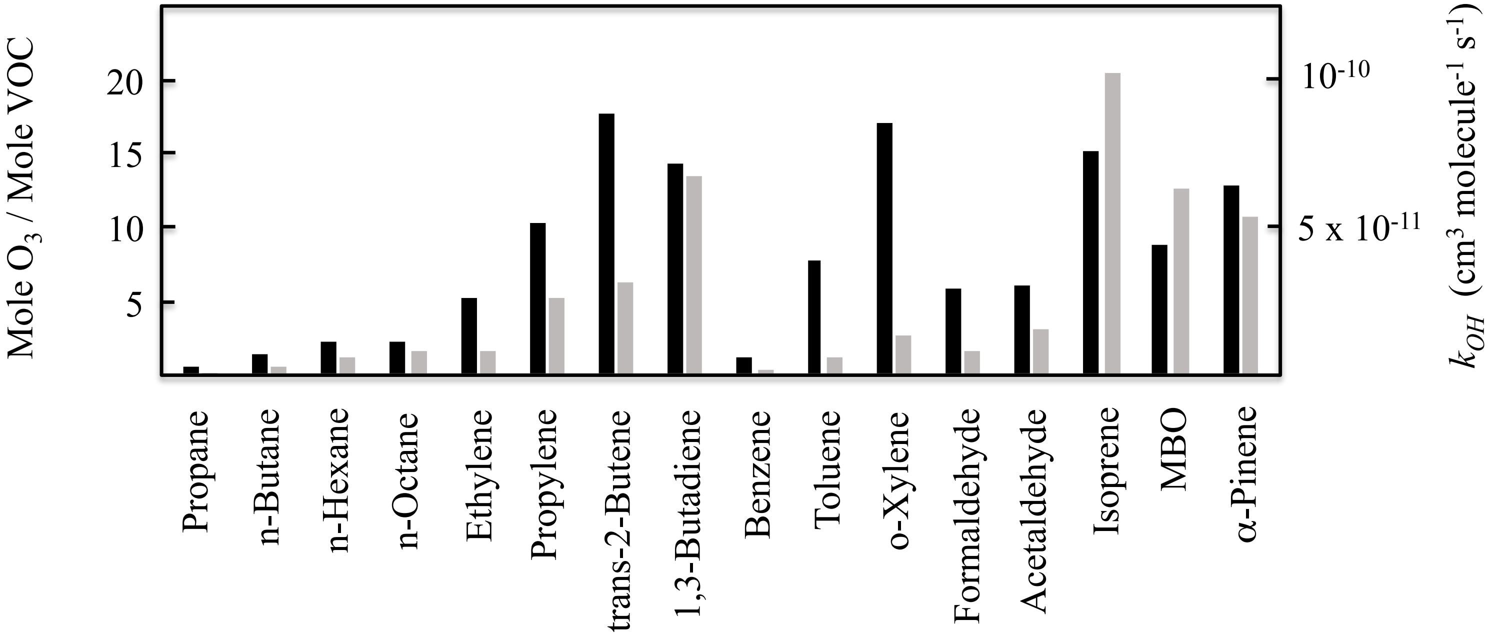
The main oxidation path is the addition of OH to the aromatic ring to form an aromatic radical. The products may (1) maintain the aromatic ring or (2) result from a break-up of the ring. Example of toluene:

(1) Toluene + OH => cresol (about 18 %)

(2) Toluene + OH => aldehydes (glyoxal, methylglyoxal, methyl butene dial, 1,4-butenedial) (> 70 %)

VOC Reactivity

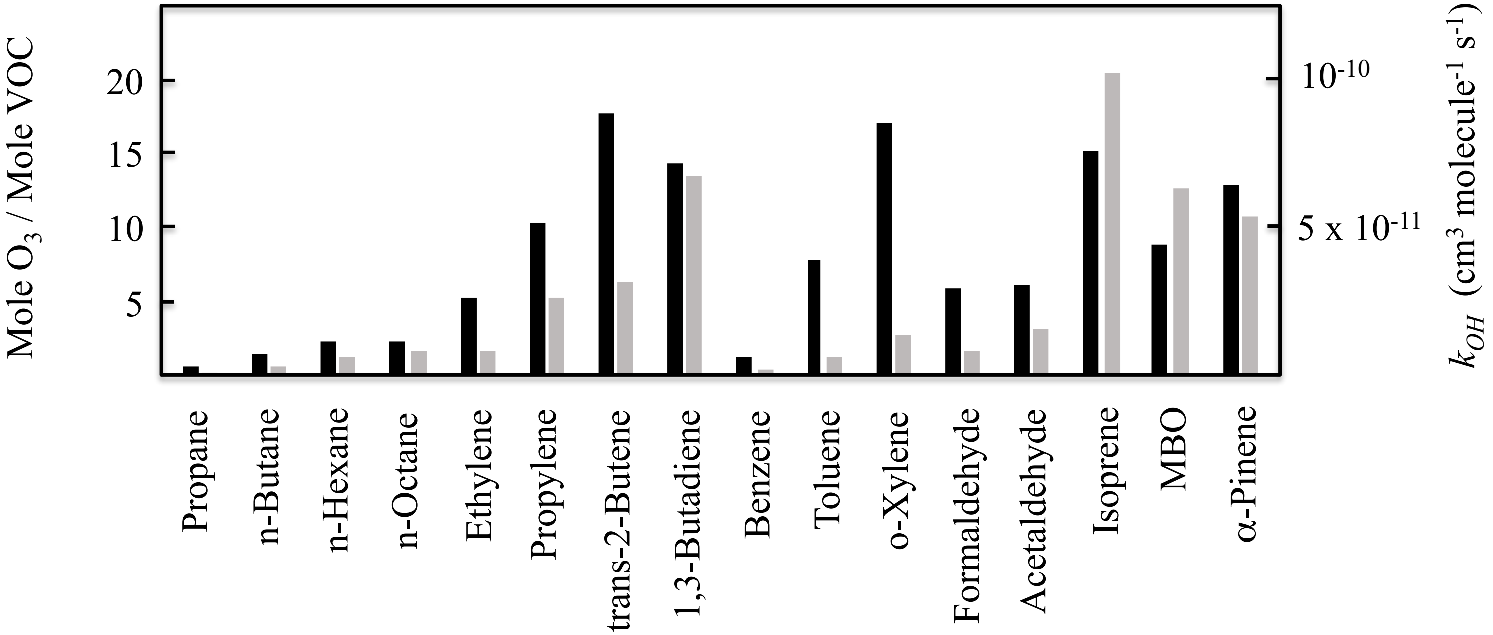
Some VOC are more reactive than others and one can define VOC reactivity scales.



Comparison of reactivity scales for VOC based on (1) “Maximum incremental reactivity” (MIR; black bars, left side scale) and (2) OH kinetics (grey bars, right side scale). The MIR can be measured in the laboratory (smog chamber experiment) or calculated with a chemical kinetic mechanisms (here, simulation with SAPRC-07, WPL Carter, Univ. of California at Riverside).

VOC Reactivity

Some VOC are more reactive than others and one can define VOC reactivity scales.



VOC reactivity is a combination of kinetics (how fast is the VOC oxidized) and mechanism (how many O_3 molecules are formed per VOC molecule oxidized).

Termination of the VOC Oxidation Cycles

The cycle is mostly catalyzed by the oxidation of NO into NO_2 and the photolysis of NO_2. Therefore, the reaction of NO_2 with a radical (OH or an organic radical) can terminate an oxidation cycle

Formation of a sink species:

$$NO_2 + OH \quad \Rightarrow HNO_3$$

Formation of a reservoir species:

$$NO_2 + CH_3C(O)O_2 \Leftrightarrow CH_3C(O)O_2NO_2 \text{ (PAN)}$$

Termination of the VOC Oxidation Cycles

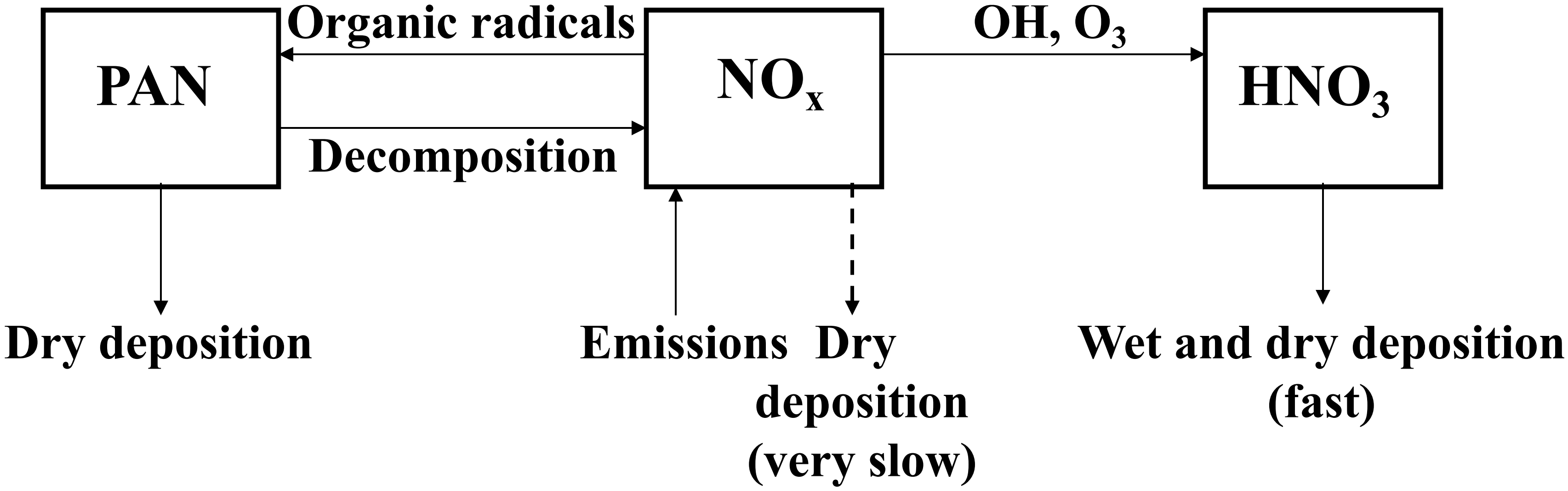
The cycle can also be terminated by reactions between peroxyl radicals

For example:

$HO_2 + HO_2$ => H_2O_2 (Hydrogen peroxide)

$HO_2 + RO_2$ => ROOH (Organic peroxide)

Nitrogen Oxides in the Atmosphere



PAN

Organic radicals

Decomposition

NO_x

OH, O_3

HNO_3

Dry deposition

Emissions

Dry deposition (very slow)

Wet and dry deposition (fast)

Chemical Regimes
NO_x-limited vs VOC-limited

- High-NO_x regime (VOC-limited): Termination occurs mostly via nitric acid (HNO_3) formation.

$$NO_2 + OH \Rightarrow HNO_3$$

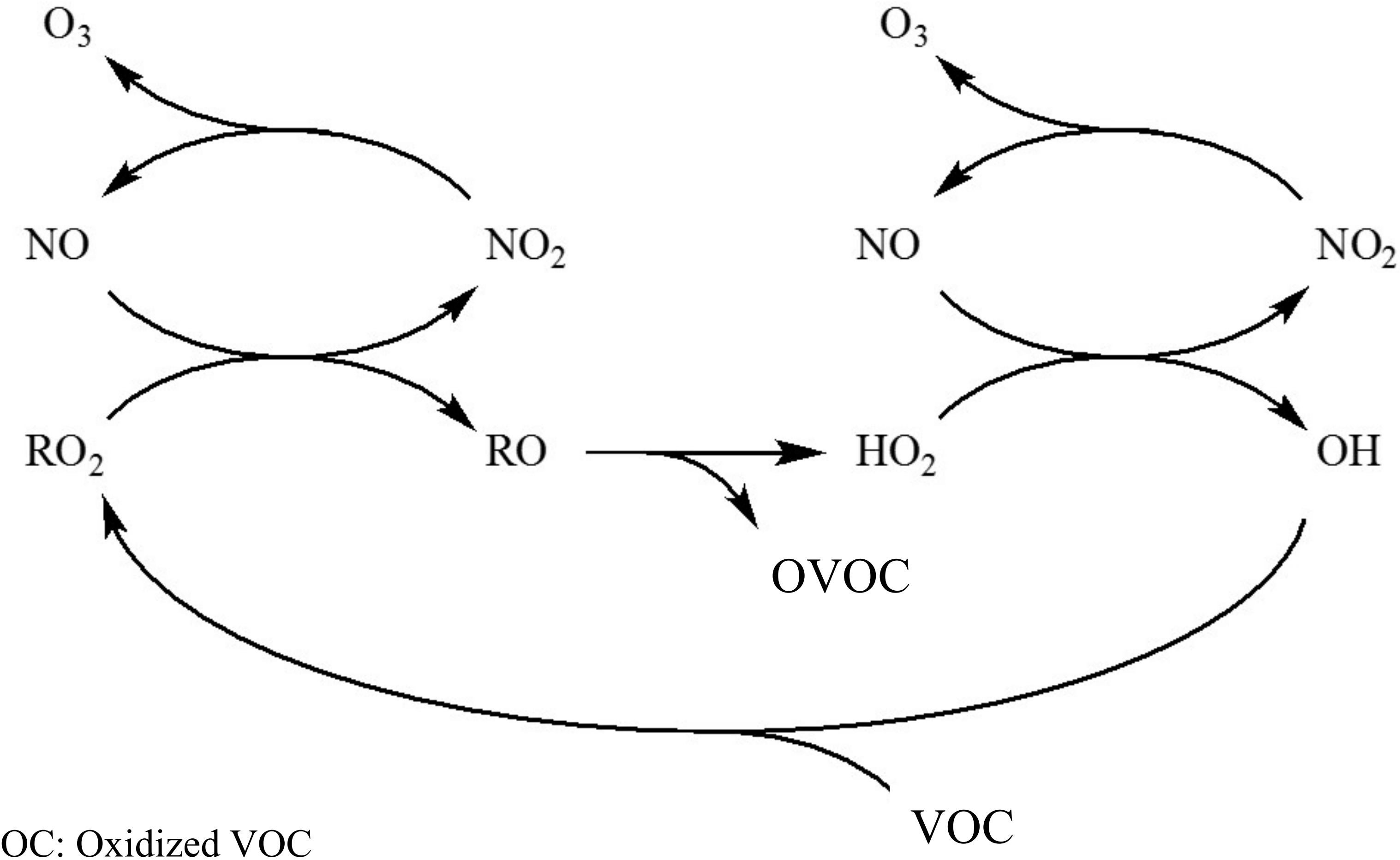
- Low-NO_x regime (NO_x-limited): The governing termination reaction is between peroxyl radicals.

$$HO_2 + HO_2 \Rightarrow H_2O_2 + O_2$$

which leads to hydrogen peroxide (H_2O_2) formation

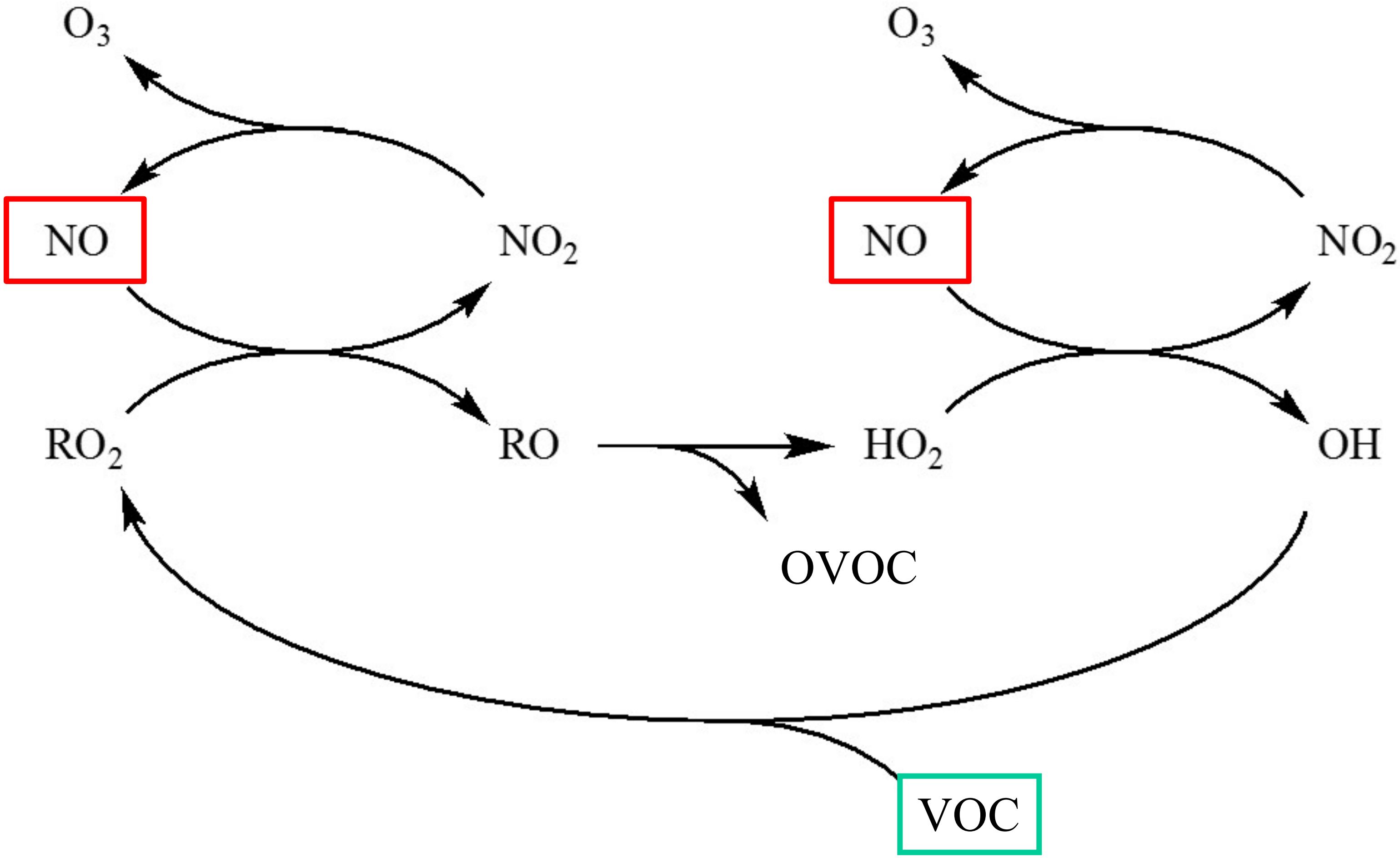
- The relative importance of the two reaction pathways depends on the [VOC]/[NO_x] ratio.

Schematic Representation of O_3 Formation

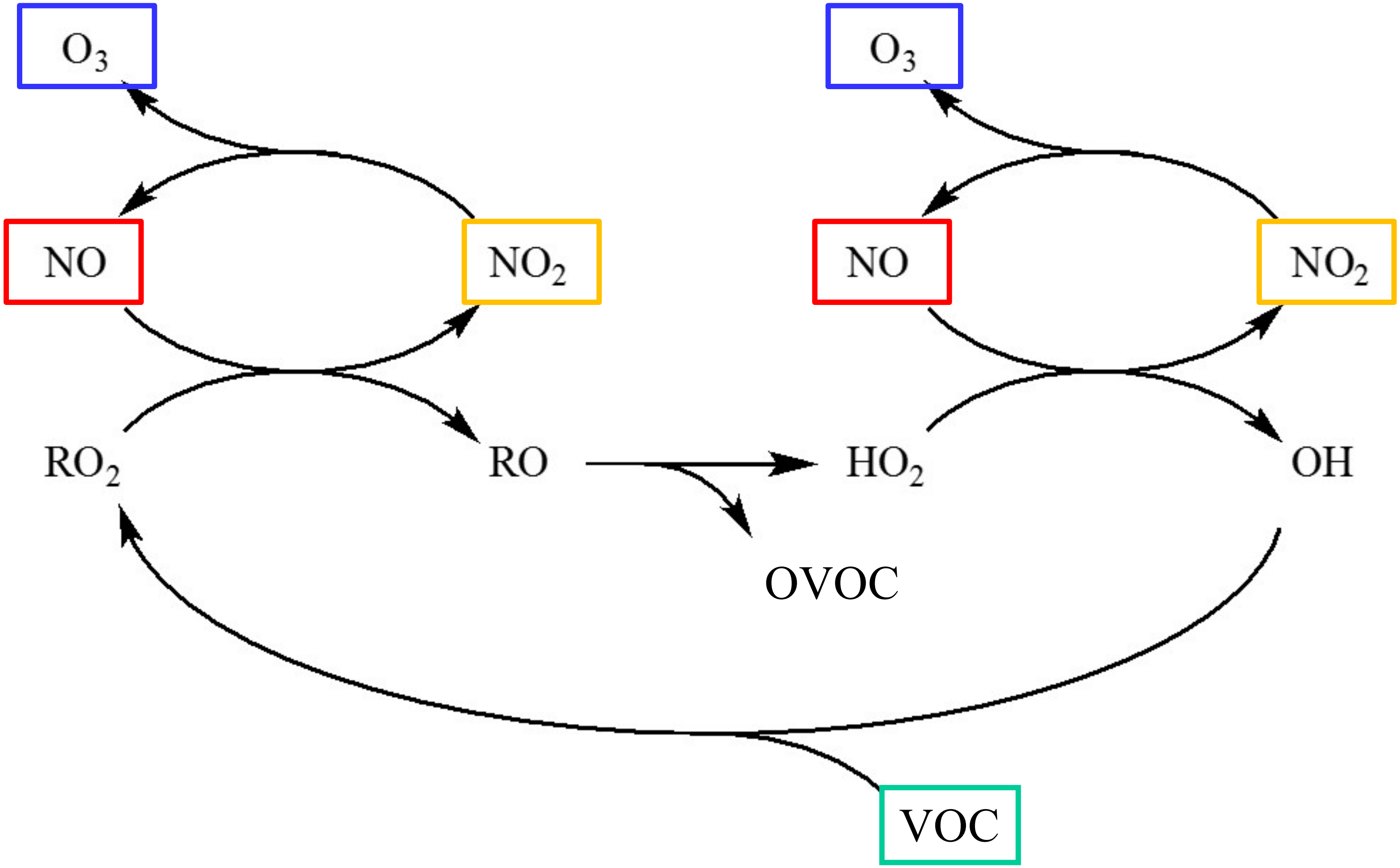


OVOC: Oxidized VOC

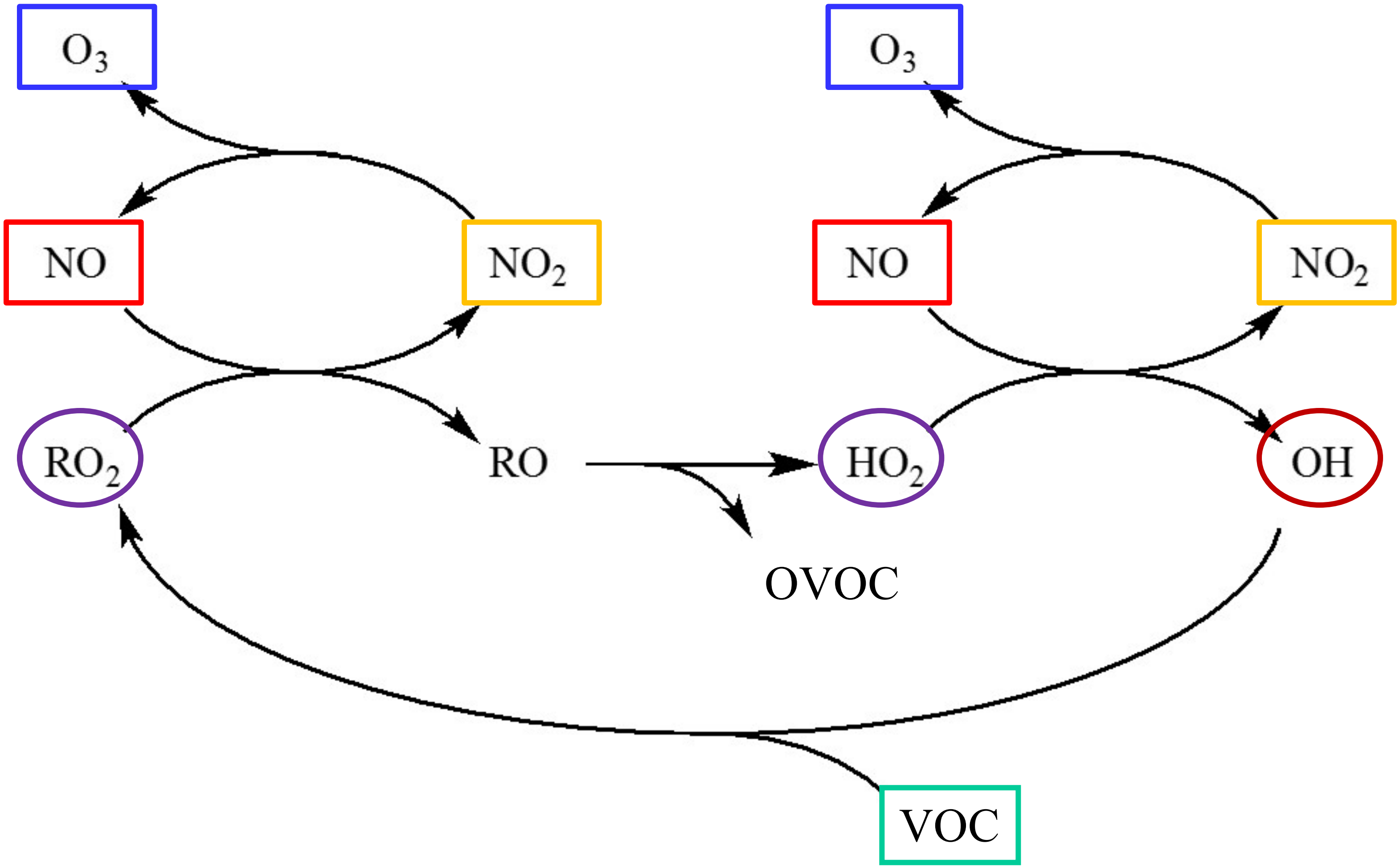
Schematic Representation of O_3 Formation Precursors: VOC and NO_x



Schematic Representation of O_3 Formation
Pollutants: O_3 and NO_2



Schematic Representation of O_3 Formation Oxidants: OH, HO_2, and RO_2



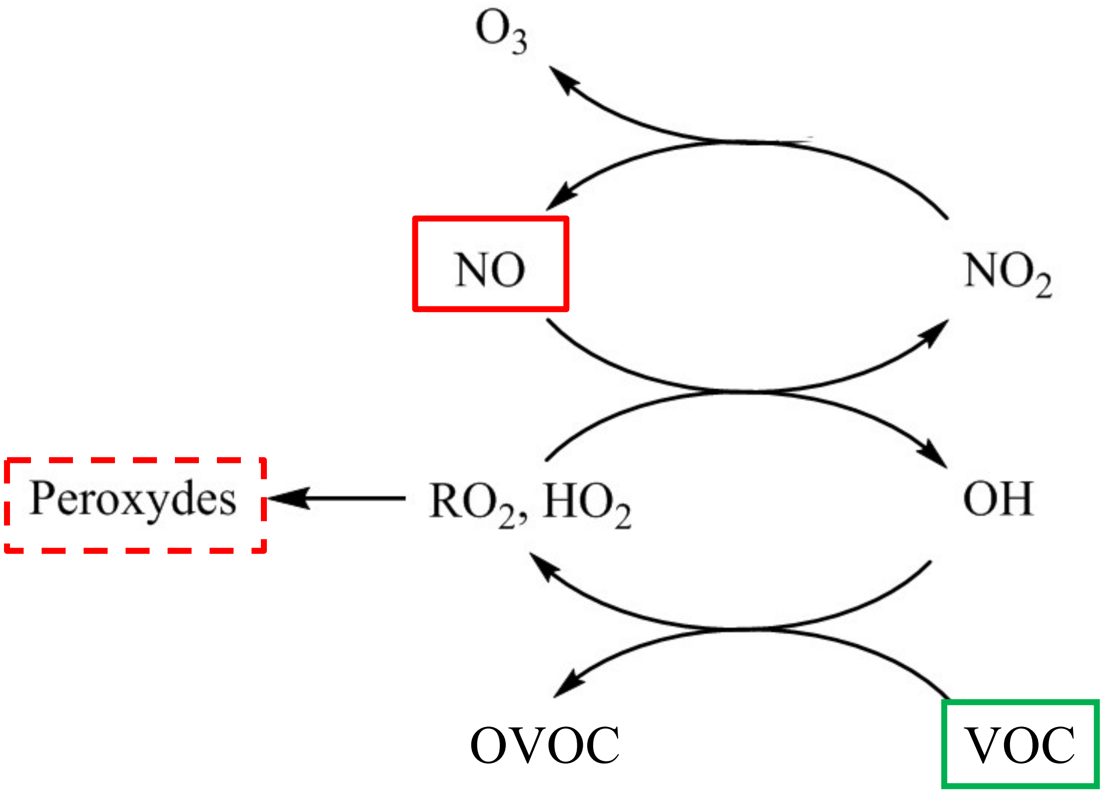
Temporal Variation of O_3 and NO_2

The O_3 maximum occurs in midday when solar radiation is the most important, thereby leading to radical formation (OH) and VOC oxidation.

The NO_2 maximum occurs in the morning during rush-hour traffic, because (1) emissions are maximum at that time and (2) during midday photolysis decreases NO_2 concentrations.

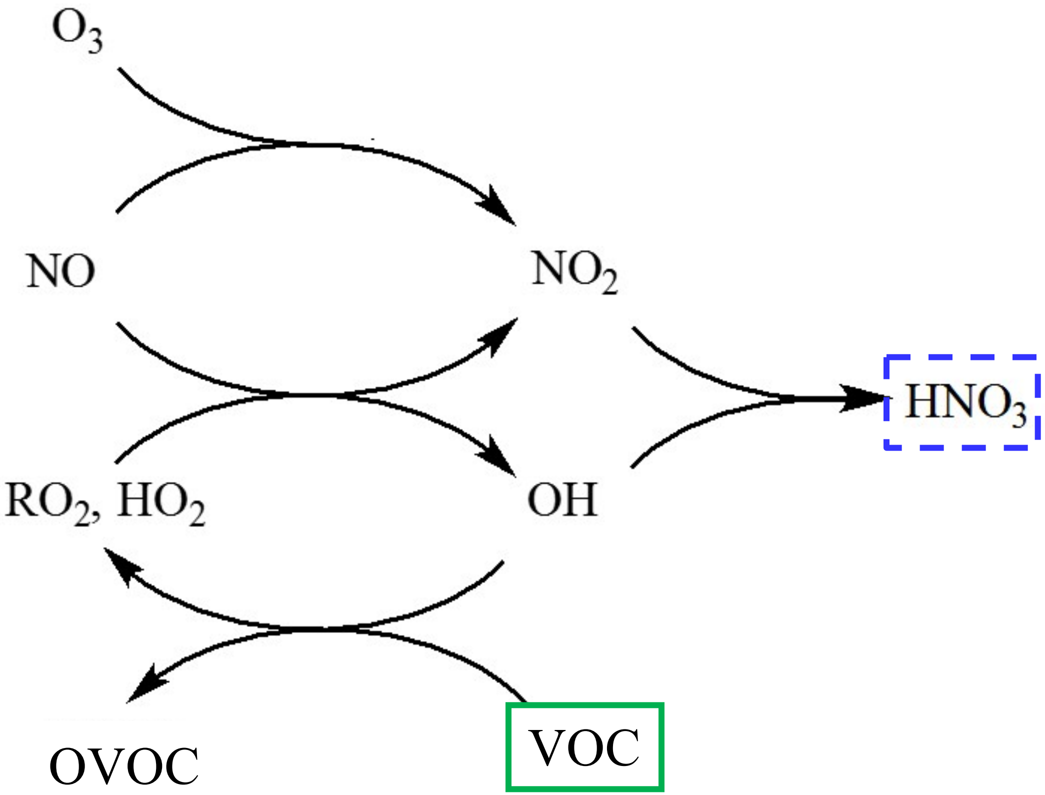
Low-NO_x Regime

In a “low-NO_x“ regime, the [VOC]/[NO_x] ratio is high and the production of peroxyl radicals RO_2 is high; therefore, NO reacts preferentially with RO_2 or HO_2 rather than with O_3 and leads to O_3 formation.



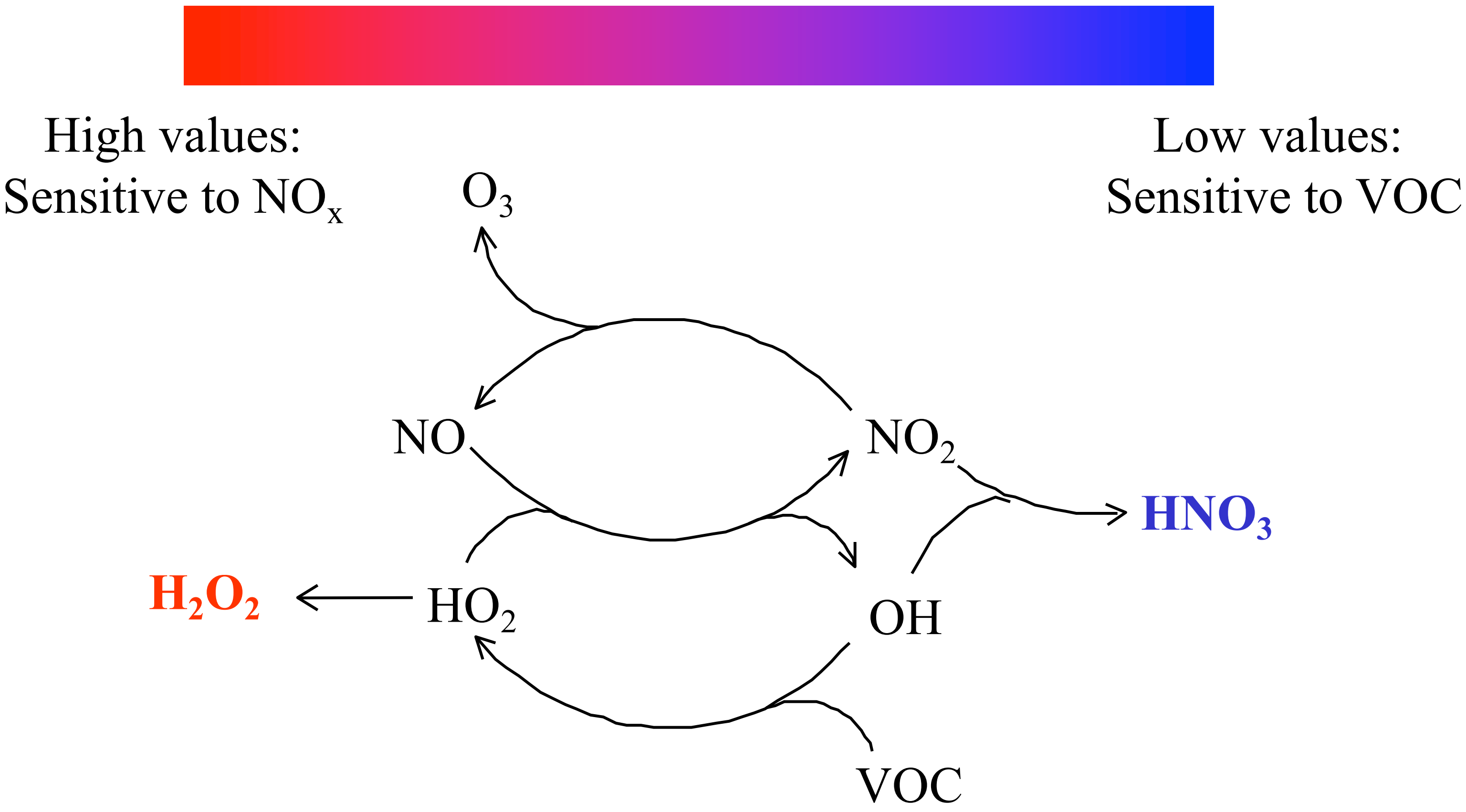
High-NO_x Regime

In a “high-NO_x“ regime, the [VOC]/[NO_x] ratio is low and the production of peroxyl radicals (RO_2) is low; therefore, NO may react preferentially with O_3 rather than with RO_2 or HO_2 and leads to O_3 destruction.



Example of "Indicators"
Sensitivity of O_3 to VOC and NO_x

- **H_2O_2 / (HNO_3 + particulate nitrate) as an indicator**



High values:
Sensitive to NO_x

Low values:
Sensitive to VOC

Chemical Regimes
NO_x-limited vs VOC-limited

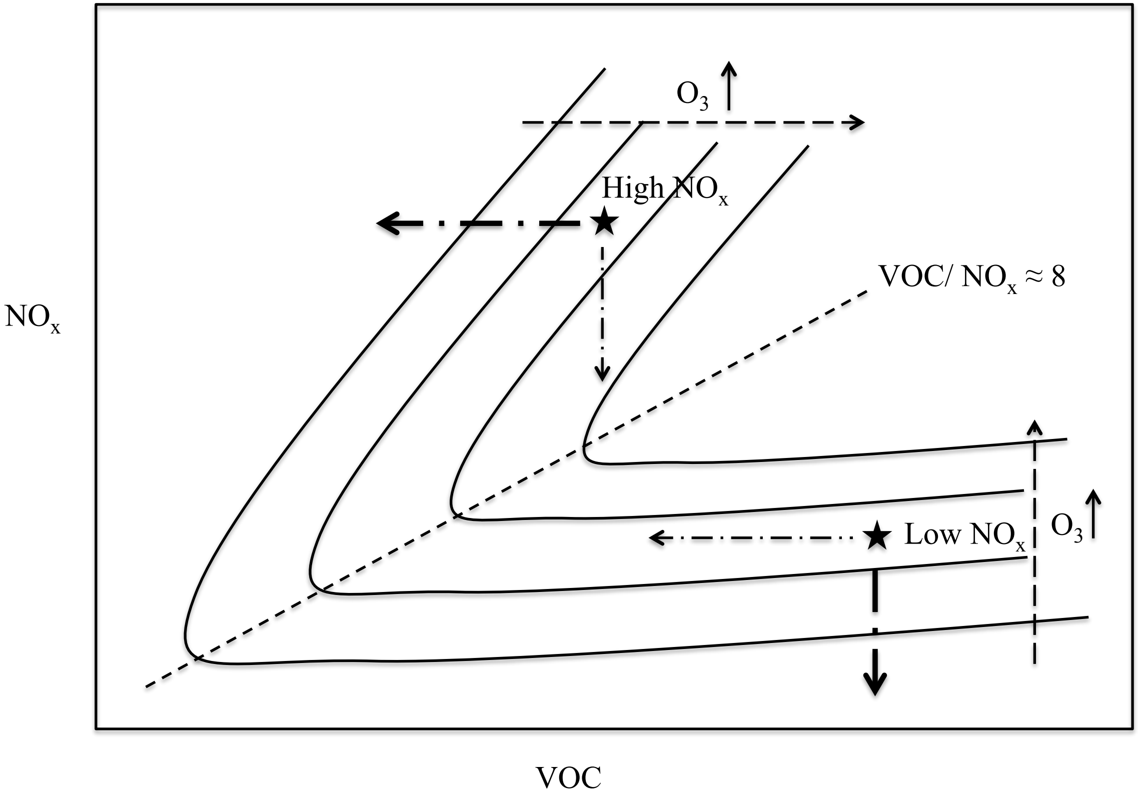
- Two chemical regimes:

  - ”Low-NO_x“ regime when NO_x concentrations are low compared to VOC concentrations (for example, remote areas): ozone formation is limited by NO_x, therefore, a reduction in NO_x leads to a reduction in ozone.

  - “High-NO_x” regime when NO_x concentrations are high compared to VOC concentrations (for example, urban areas): ozone formation is limited by VOC, therefore, a reduction in VOC leads to a reduction in ozone and a reduction in NO_x may lead to an increase in ozone.

Chemical Regimes
NO_x-limited vs VOC-limited

Isopleths of ozone (lines of constant ozone concentration, typically for the maximum daily regulatory value, i.e., 8-hour average maximum) as a function of the emissions (or early-morning concentrations) of NO_x and VOC.



The Weekend Effect

- The change in the [VOC]/[NO_x] ratio between week days and weekends affects ozone formation (fewer diesel trucks on weekends in the U.S.)

- The lower NO_x emissions on weekends lead to more ozone formation in a high-NO_x regime: this has been observed for example in Los Angeles and Chicago

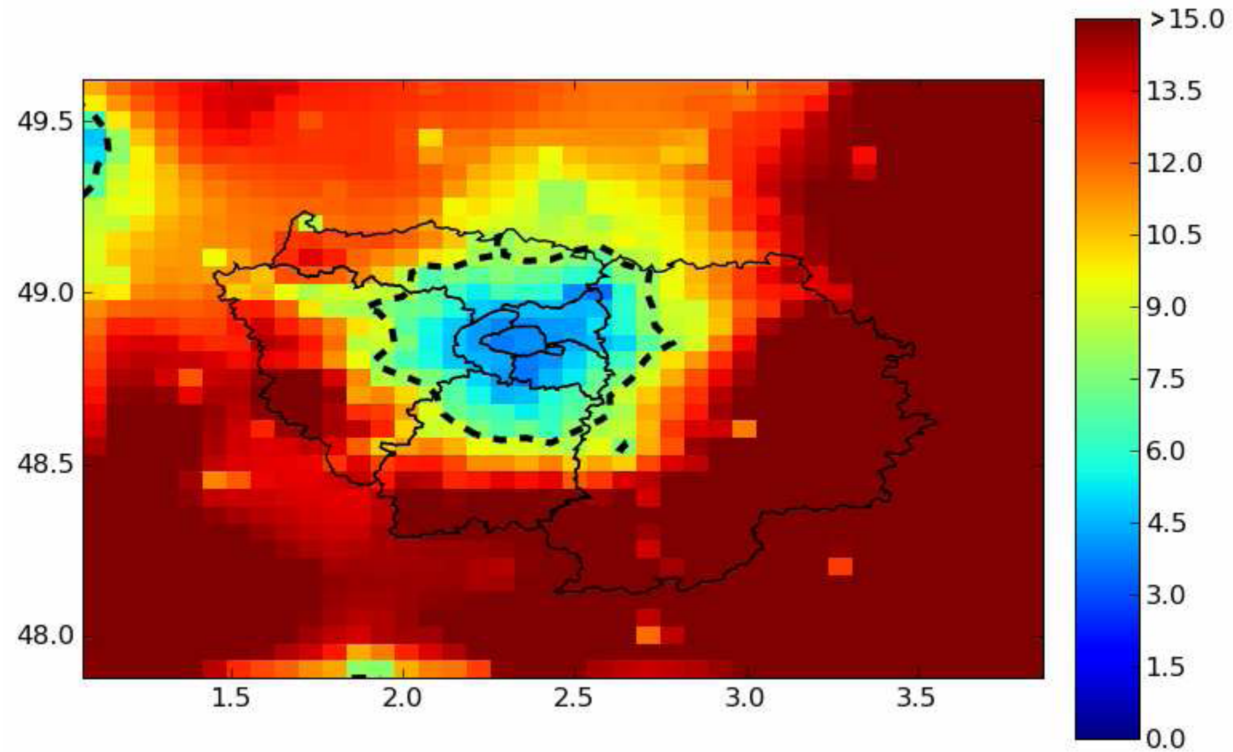
- Air quality model simulations reproduce this weekend effect (e.g., in the Los Angeles basin)

Strategy for Reducing Ozone Precursors

- Developing an effective emission control strategy is complex because the chemical regime for ozone formation varies in space and time.

- Typically (but not always)
  - Ozone formation is VOC-limited in urban areas
  - Ozone formation is NO_x-limited in rural areas

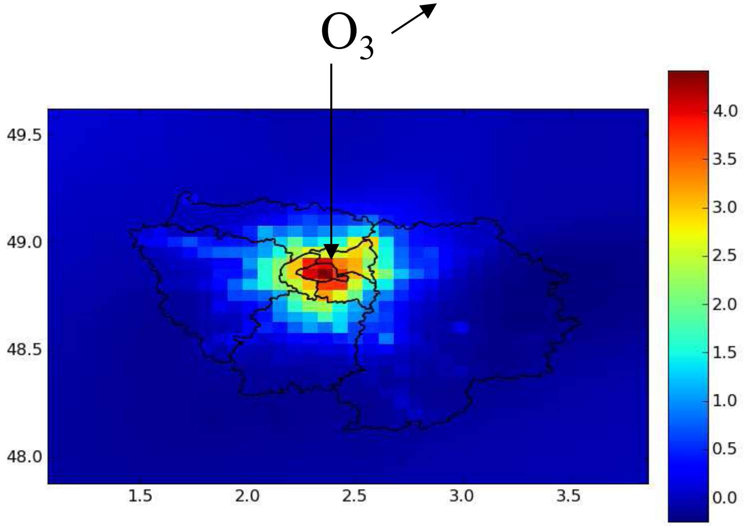
Strategy for Reducing Ozone Precursors



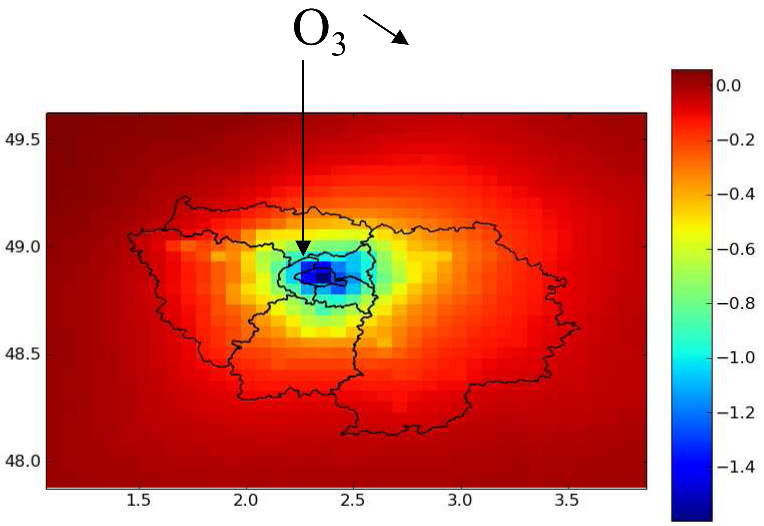
VOC / NO_x ratio calculated with a model simulation (Polyphemus model of Cerea).

The dotted line corresponds to $[VOC]/[NO_x] = 8$ and depicts the approximate boundary between the NO_x and VOC-limited regimes; VOC limited in blue/green and NO_x limited in red/yellow. Source: Cerea

Strategy for Reducing Ozone Precursors



NO_x emission reduction

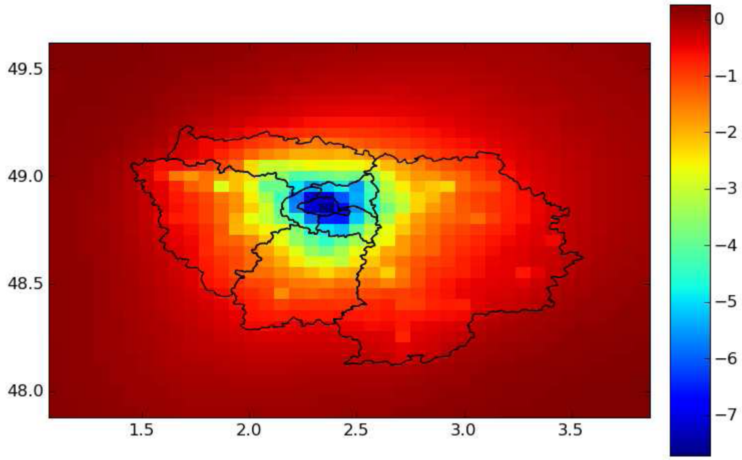


VOC emission reduction

Model simulation results (Polyphemus model of Cerea) :
Effect of 15 % reductions in NO_x or VOC emissions over the Paris region on maximum 8-hour average O_3 concentrations (µg/m^3)

Source: Cerea

Importance of Long-Range Atmospheric Transport for the Paris Region



VOC reduction

Emissions : -15 %

↓

Concentrations : -7 %

Model simulation results (Polyphemus model of Cerea) :
Relative decrease (%) of VOC concentrations due to a 15 % decrease of VOC emissions in the Paris region

Source: Cerea

The Role of Long-Range Transport on Ozone Concentrations

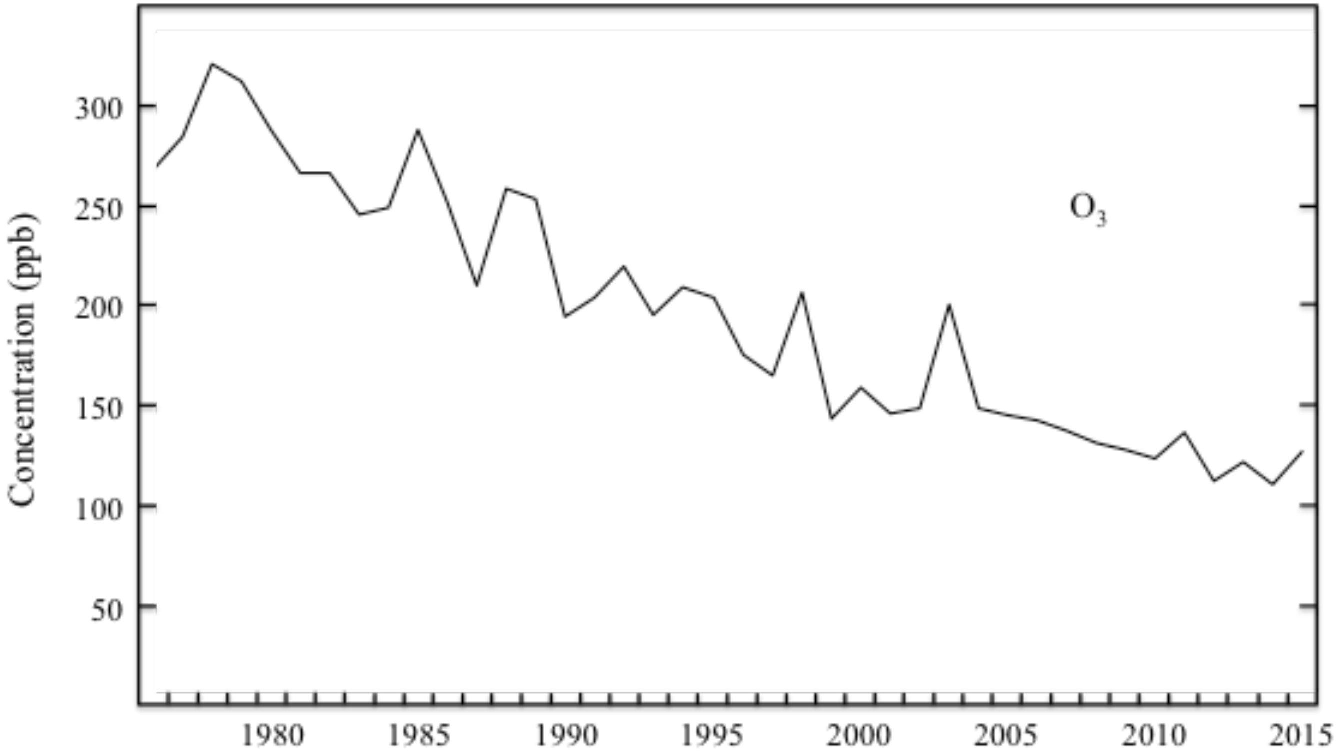
- Lifetime of ozone: one to two weeks => trans-Pacific Ocean and trans-Atlantic Ocean transport

- Some studies estimate that
  - 5 to 10 ppb of ozone concentrations in California are due to Asian emissions (mostly in April and May)
  - 3 to 5 ppb of ozone concentrations in western Europe are due to North American emissions

- Challenge: local emissions must decrease sufficiently to account for the potential increase of the global ozone background concentrations.

Evolution of Ozone Concentrations in Los Angeles, California

Significant decrease of ozone concentrations in Los Angeles (with inter-annual variability)



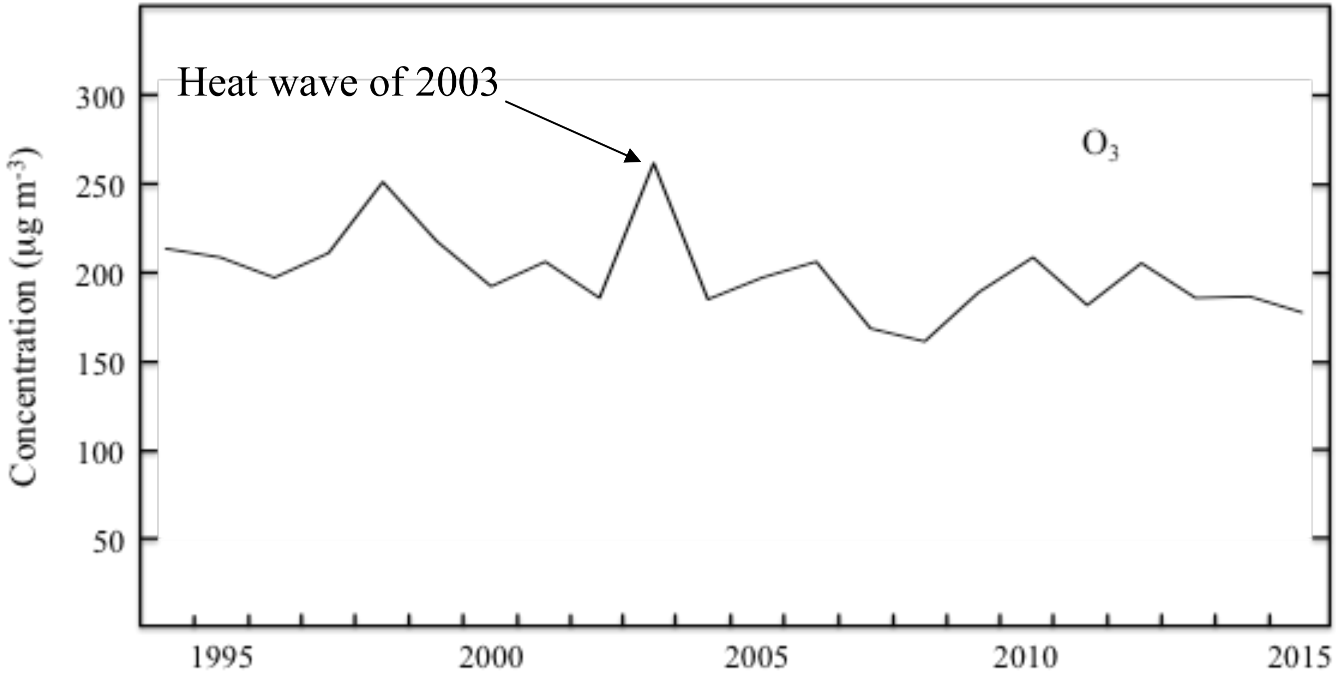
Maximum 8-hour average concentrations

(Regulatory value: 70 ppb averaged over 8 hours, to be exceeded 3 times)

Source: SCAQMD, http://www.aqmd.gov

Evolution of Ozone Concentrations in Paris

Little decrease of ozone concentrations in Paris
(with inter-annual variability)



Maximum 8-hour average concentrations
(Regulatory value: 120 µg/m^3 averaged over 8 hours, to be exceeeded 25 times)

Source: AIRPARIF, http://www.airparif.asso.fr

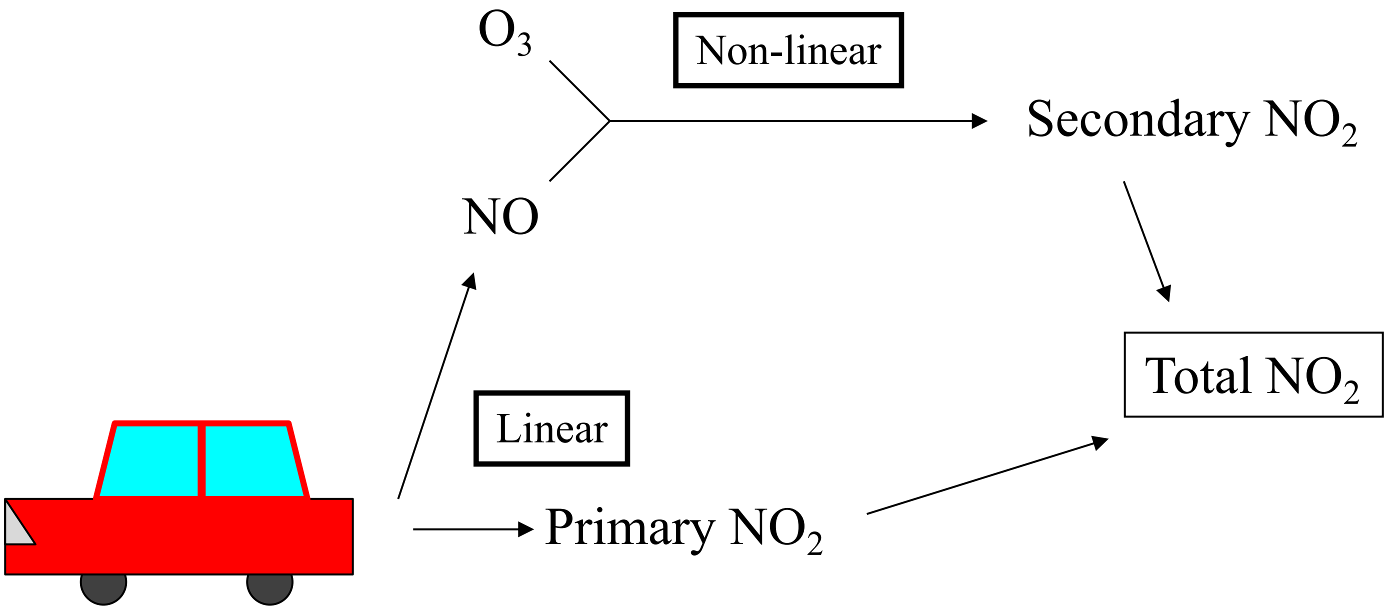
Evolution of Ozone Concentrations in Paris

Possible explanations

- **Chemistry:** Joint reductions in NO_x and VOC emissions led to little change in the VOC/NO_x ratio and, therefore, little change in ozone concentrations.

- **Physics (Long-range transport)**: The limited decrease in ozone concentrations overall in Europe leads to a nearly constant ozone background, which contributes significantly to ozone concentrations in the Paris region.

Primary and Secondary NO_2



O_3

Non-linear

Secondary NO_2

NO

Total NO_2

Linear

Primary NO_2

Evolution of NO_2 Concentrations in Paris

Two hypotheses:

- Secondary NO_2: NO_2 is formed by reaction of NO with O_3; as O_3 decreases little, NO_2 decreases little (there is more NO than O_3, therefore, O_3 is the limiting species for NO_2 formation).

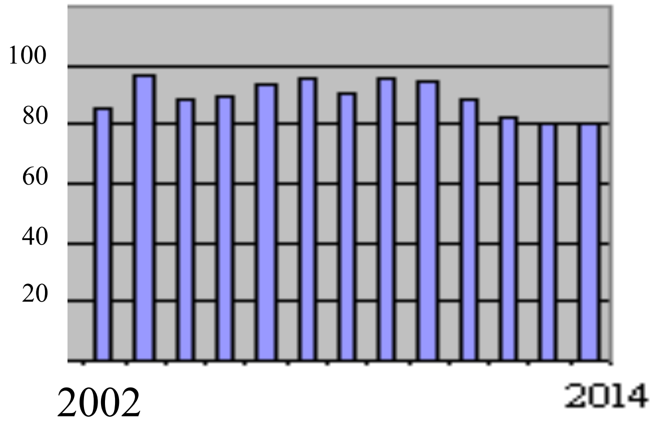
- Primary NO_2: The NO_2 fraction in NO_x emissions increased because of the effect of some particle diesel filters on NO oxidation to NO_2.

Evolution of NO_2 Concentrations in Paris

Simulations conducted at Cerea suggest that the first hypothesis (greater NO_2 fraction in NO_x emissions) is the most likely (Roustan et al., *Atmos. Environ.*, 2011)

The use of diesel particle filters in some diesel vehicles has led to an increase of the NO_2 fraction in NO_x emissions; as a result, NO_2 concentrations in the Paris region remained nearly constant for several years. Nevertheless, they have started to decrease.

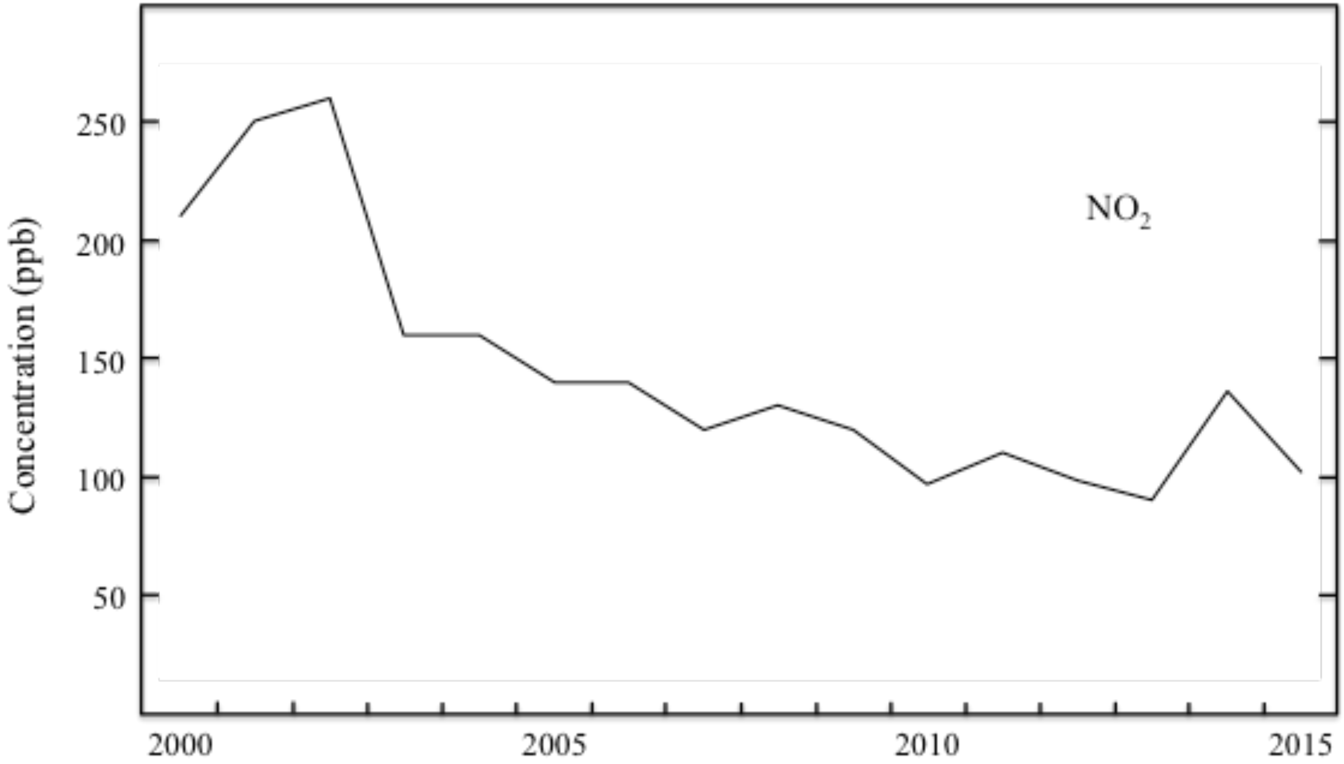
Annual concentrations of NO_2 ($\mu g/m^3$) at a near-road monitoring station in the Paris region



Source of data: Airparif

Evolution of NO_2 Concentrations in Los Angeles, California

Significant decrease (3 % per year) of NO_2 hourly concentrations in Los Angeles (with inter-annual variability)



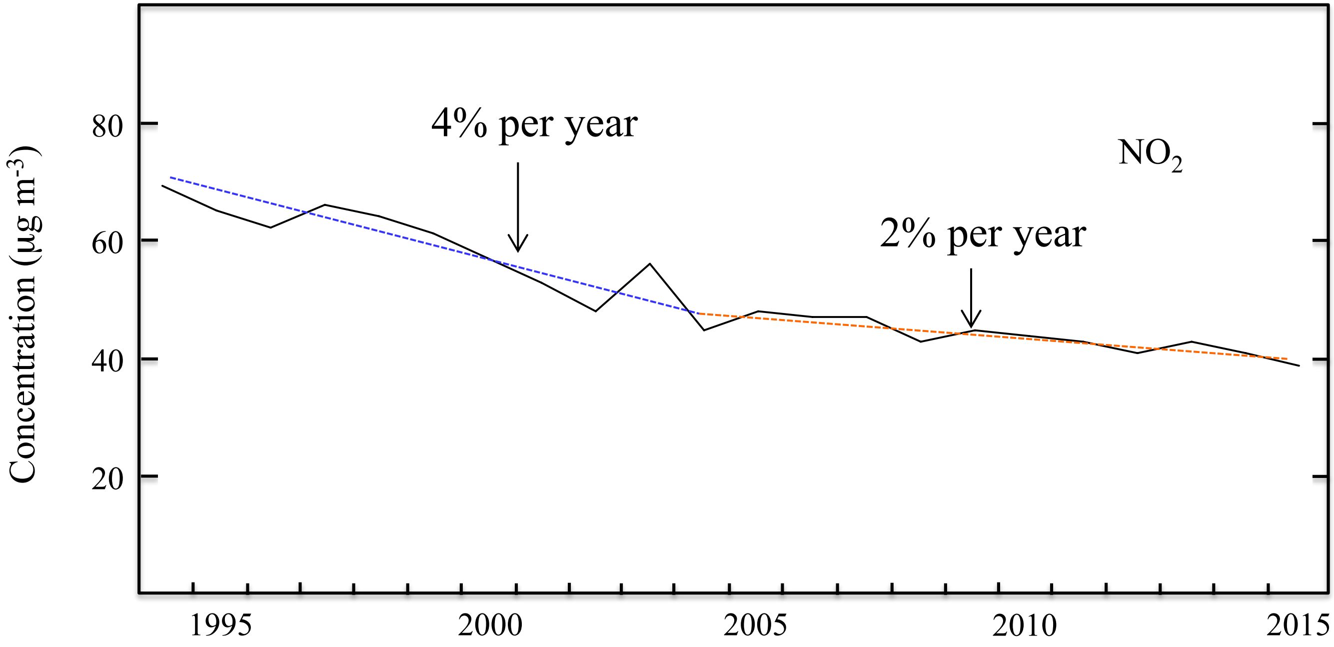
Maximum 1-hour average concentrations

(Regulatory value: 100 ppb averaged over 1 hour, to be exceeded 7 times)

Source: SCAQMD, http://www.aqmd.gov

Evolution of NO_2 Concentrations in Paris

Significant decrease (3 % per year) of NO_2 annual concentrations in Paris over the long term (with inter-annual variability)



Maximum annual average background concentrations
(Regulatory value: 40 µg/m^3)

Source: AIRPARIF, http://www.airparif.asso.fr

Chemical Mechanisms of Photochemical Air Pollution

A chemical kinetic mechanism must represent the reactions that take place among the different chemical species and correctly simulate the evolution of the concentrations of the main air pollutants.

The chemical kinetic mechanism must be incorporated into an air quality model that simulates also the atmospheric transport processes (chemical-transport model or CTM); therefore, it is necessary to have an efficient numerical scheme for the chemical kinetic equations.

Chemical Mechanisms of Photochemical Air Pollution

- Mechanism for inorganic chemistry (NO_x, SO_2, CO, O_3, etc.)
  - About 20 species and 50 reactions
- Detailed mechanisms for organic chemistry (VOC)
  - Several hundreds of species and several thousands of reactions
- Reduced mechanisms for organic chemistry
  - 30 to 100 species and about one to three hundred reactions

Chemical Mechanisms of Photochemical Air Pollution

- Two main categories of mechanisms for VOC
- Mechanisms with surrogate molecular species: SAPRC99, RACM, RACM2, MELCHIOR, CACM…
- Mechanisms based on the decomposition of organic chemical species into functional groups (“carbon-bond” mechanisms): CBIV, CB05…

Mechanisms with Surrogate Species

Example of RACM2:

- n-butane : HC3 (alkanes, alcohols, esters, and alkynes with a rate constant for reaction with OH < 3.4 x 10^{-12} cm^3 s^{-1})

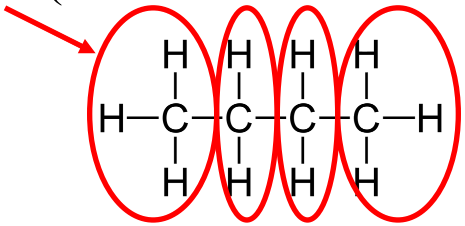
- 1-hexene : OLT (terminal alkenes)

- propionaldehyde : ALD (aldehydes with 3 carbons or more)

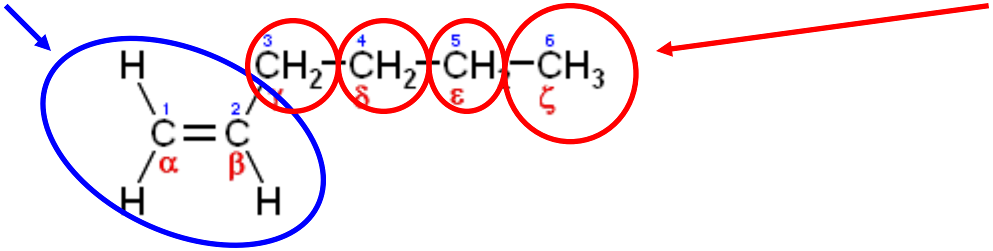
Carbon-Bond Mechanisms

Example of CB05:

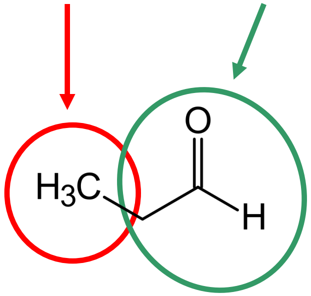
- n-butane: 4 PAR (carbon atoms with single bonds)



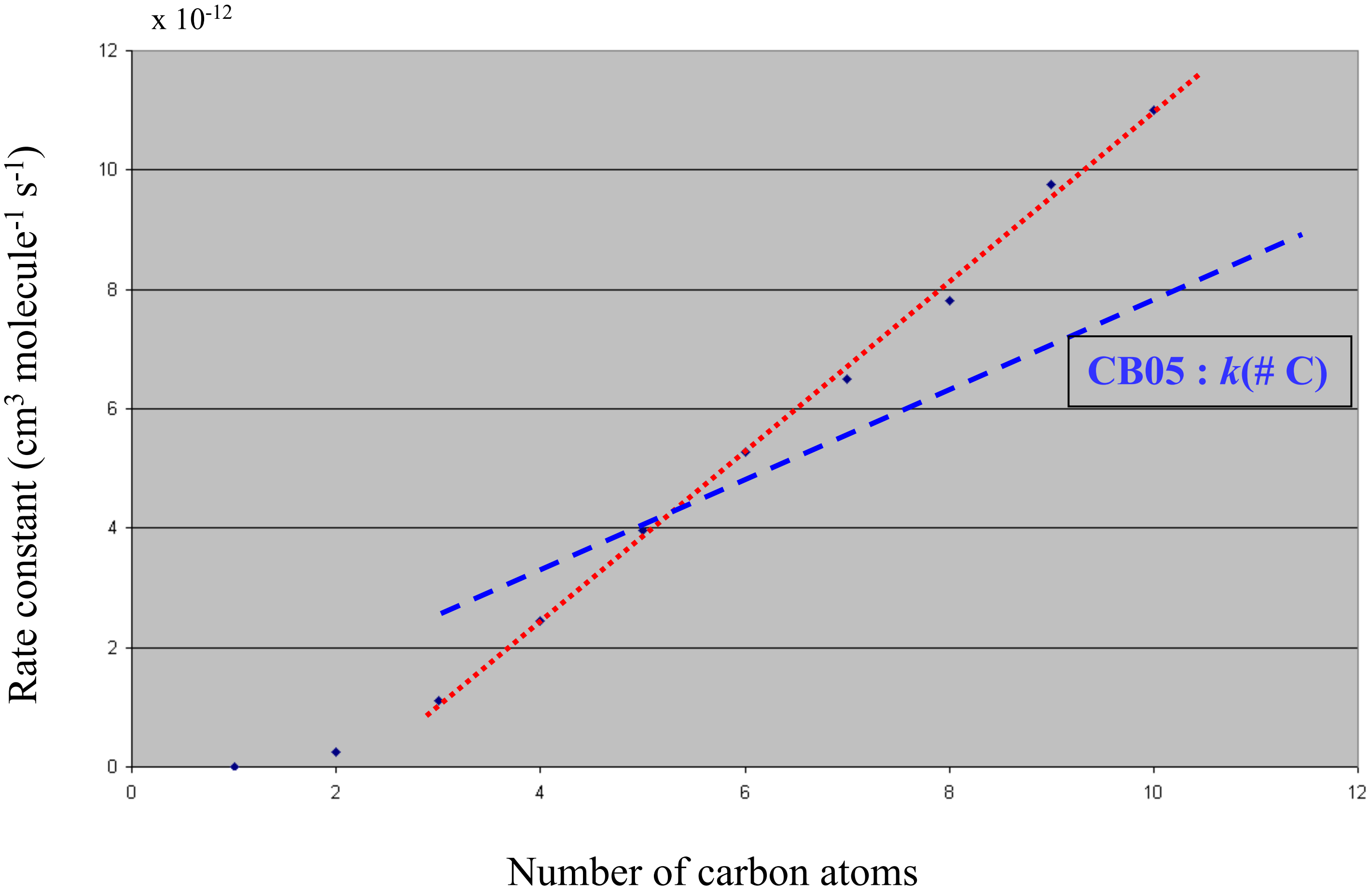
- 1-hexene: 1 OLE (2 carbon atoms with a double bond) + 4 PAR



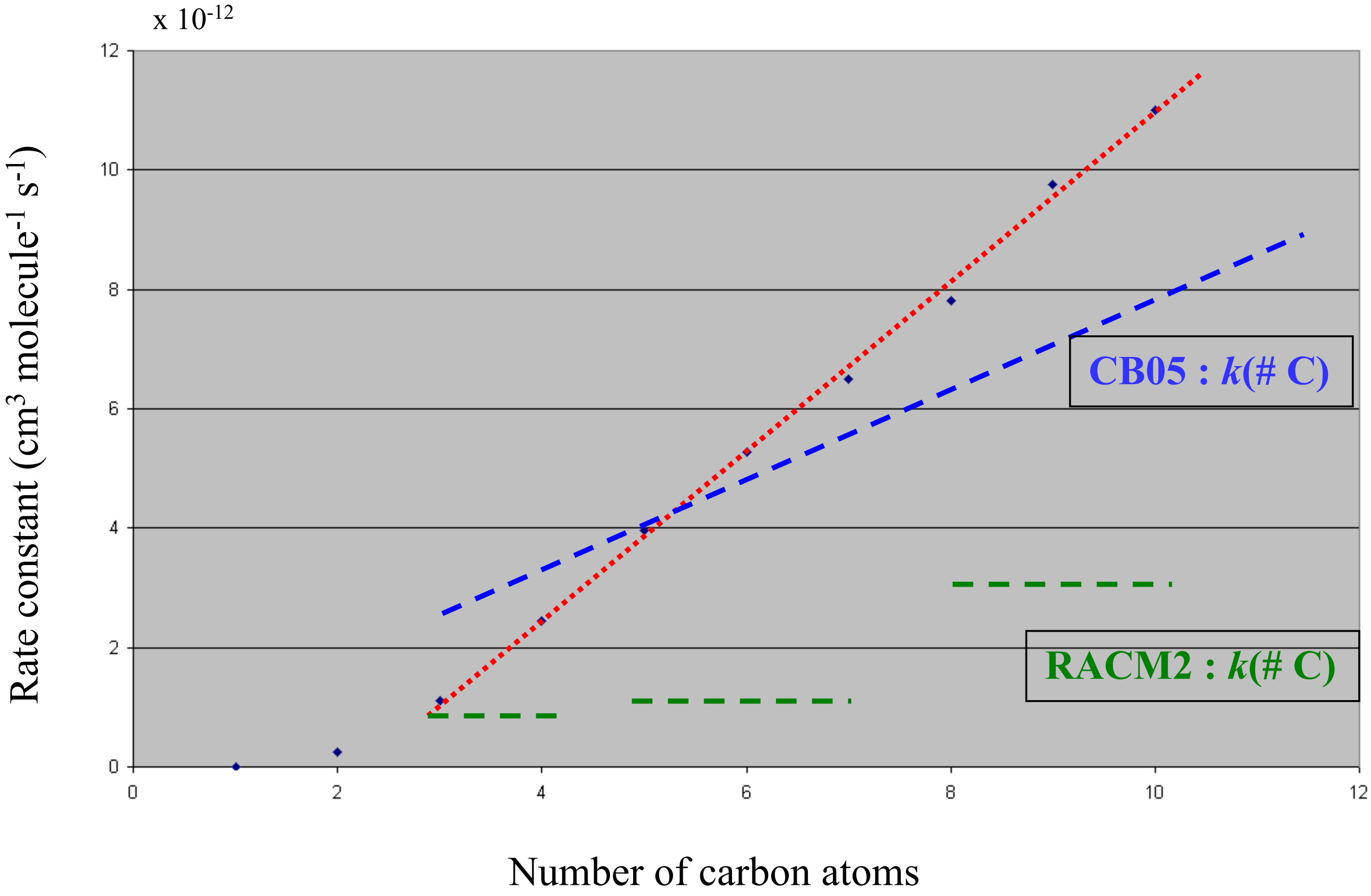
- propionaldehyde: 1 PAR + 1 ALDX (acetaldehyde)



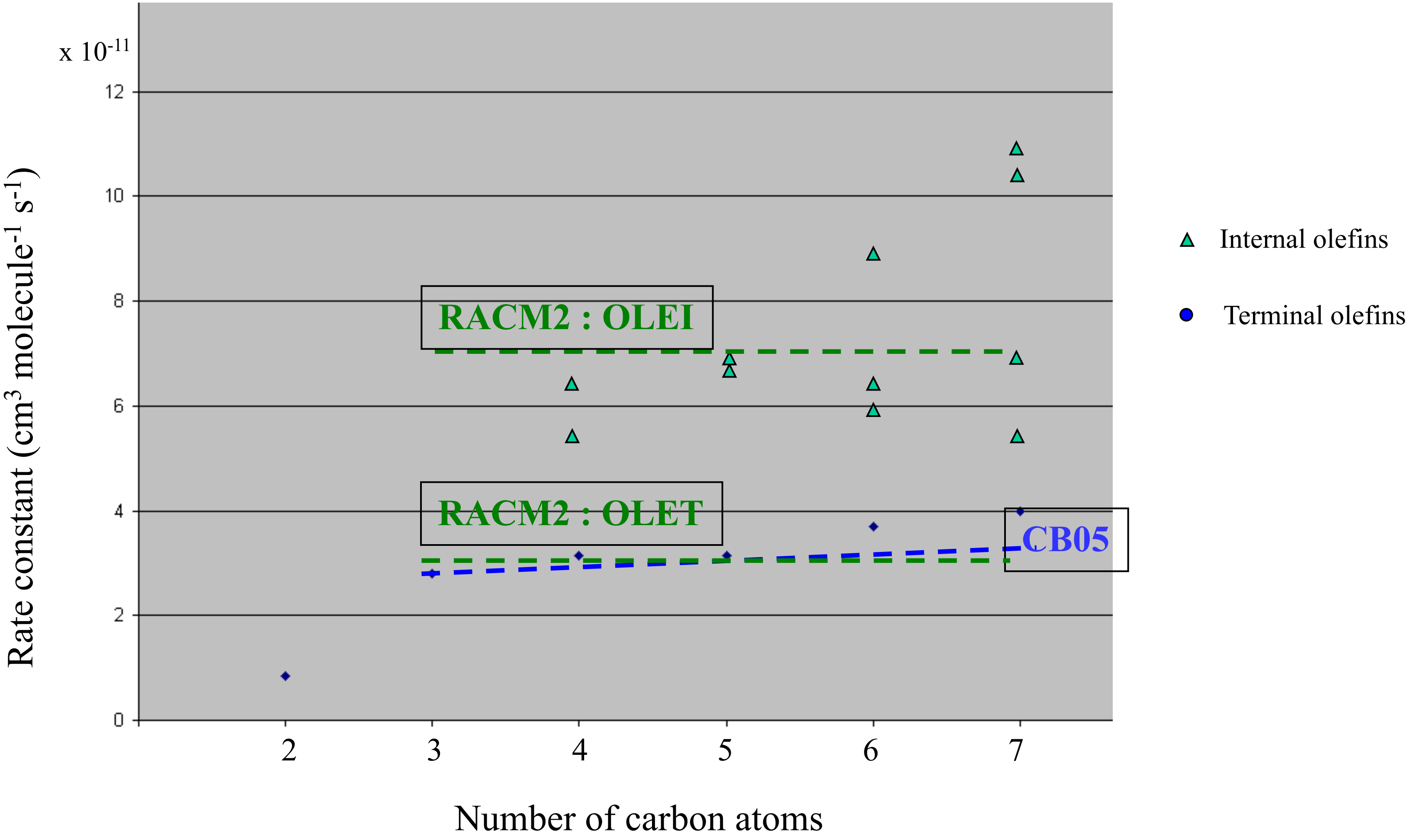
Kinetics of Oxidation of Alkanes by OH



Kinetics of Oxidation of Alkanes by OH



Kinetics of Terminal and Internal Alkene Oxidation by OH



Chemical Mechanisms of Photochemical Air Pollution

Chemical kinetic mechanisms are evaluated against experimental data obtained in smog chambers.

Those smog chambers may be indoor or outdoor, small or large, in Teflon or stainless steel…

If needed, the chemical kinetic mechanism is improved to obtain better agreement with the experimental data