Tropospheric Oxidation & Ozone Formation I

<u>Required</u> Reading: Jacob Chapters 11 & 12

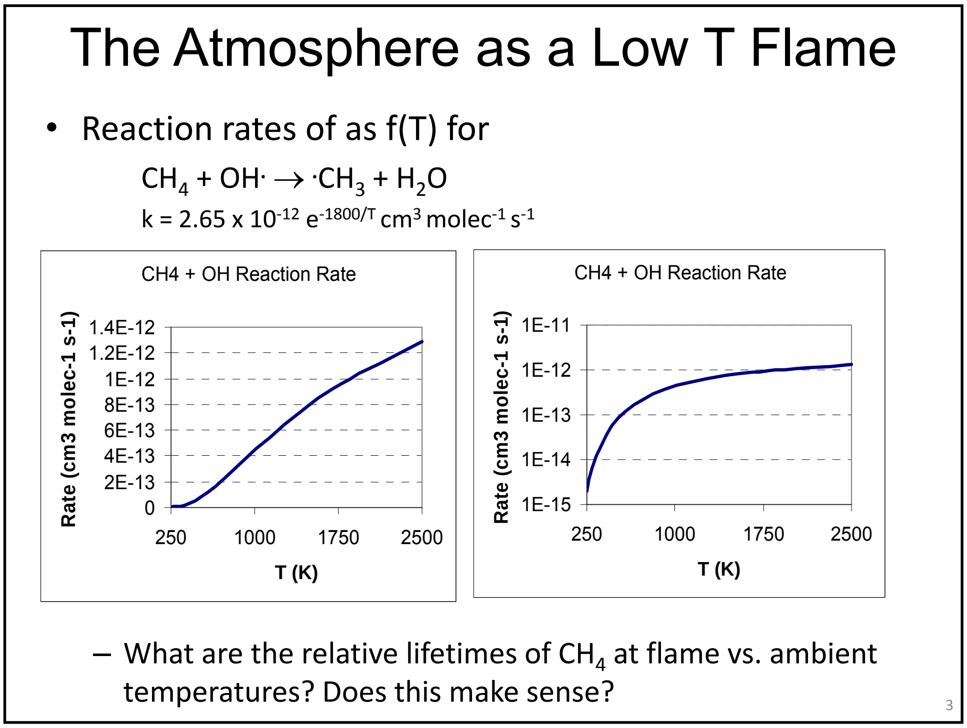
Atmospheric Chemistry
ATOC-5151 / CHEM 5151
Prof. Jose-Luis Jimenez
Spring 2013
Lecture by Doug Day

Review Clicker Q

What are the most important sources of tropospheric hydroxyl radicals (OH)?

(in no particular order)

a) CH_2O, HONO, HCl
b) O_3, HNO_3, CH_2O
c) HONO, CH_2O, O_3
d) CH_4, O_3, HONO
e) I don't know



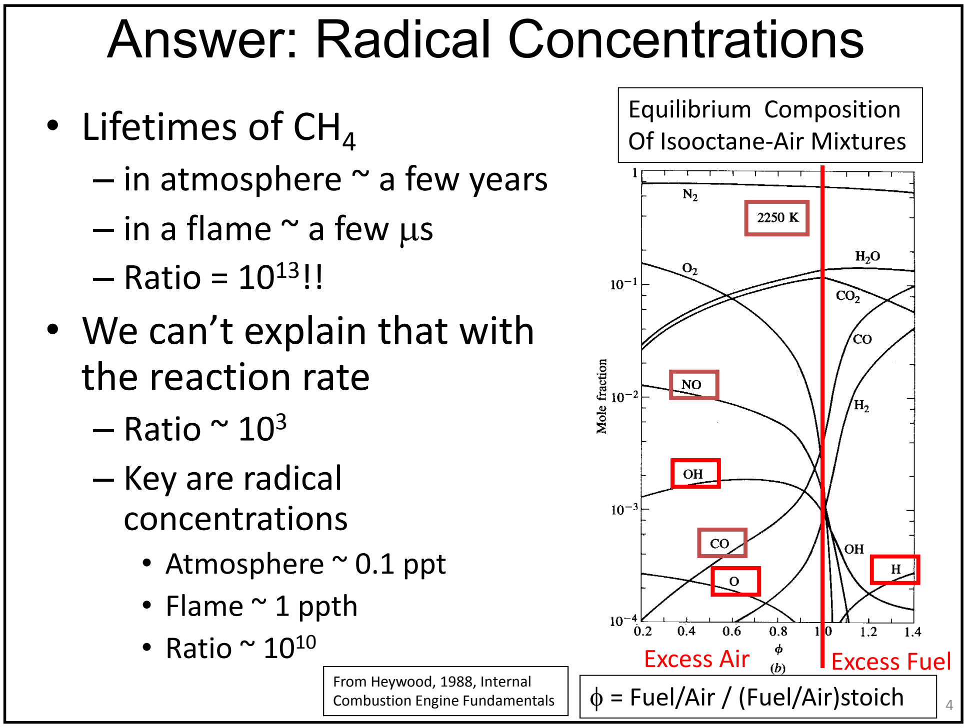
The Atmosphere as a Low T Flame

- Reaction rates of as f(T) for

$CH_4 + OH\cdot \rightarrow \cdot CH_3 + H_2O$

$k = 2.65 \times 10^{-12}\, e^{-1800/T}\ \mathrm{cm^3\ molec^{-1}\ s^{-1}}$

  - What are the relative lifetimes of CH_4 at flame vs. ambient temperatures? Does this make sense?



Answer: Radical Concentrations

- Lifetimes of CH_4
  - in atmosphere ~ a few years
  - in a flame ~ a few μs
  - Ratio = 10^{13}!!
- We can't explain that with the reaction rate
  - Ratio ~ 10^3
  - Key are radical concentrations
    - Atmosphere ~ 0.1 ppt
    - Flame ~ 1 ppth
    - Ratio ~ 10^{10}

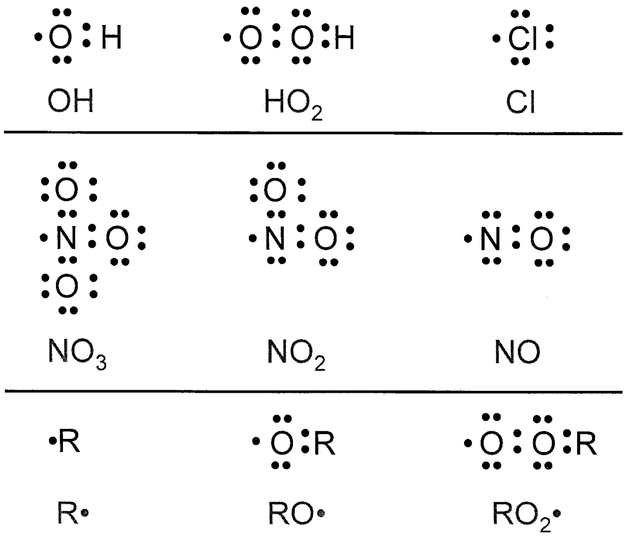
Equilibrium Composition
Of Isooctane-Air Mixtures

From Heywood, 1988, Internal Combustion Engine Fundamentals

ϕ = Fuel/Air / (Fuel/Air)stoich

Radicals

- Radical = species with an unpaired electron
  - High energy, high tendency to pair the electron to reduce the free energy
  - Often rapid reactions



Adapted from Paul Ziemann

Dominant Oxidant Source in Troposphere

Hydroxyl Radical (OH) Production from Ozone:

Photodissociation of O_3:

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

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

NET: $O_3 + h\nu + H_2O \rightarrow O_2 + 2OH\cdot$

Sources of Ozone:

- Stratospheric transport
- Tropospheric photochemical production

O(^{1}D) in the Troposphere

Production & Losses of OH, O(^{1}D)
(new reactions from homework #5)

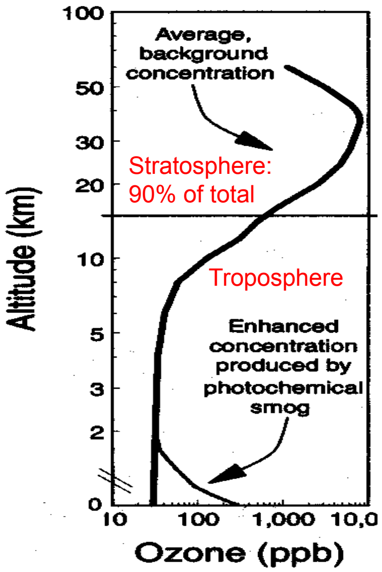
$O_3 + h\nu \rightarrow O(^1D) + O_2$ (4)
$O(^1D) + H_2O \rightarrow 2\ OH$ (5)
$O(^1D) + O_2 \rightarrow O(^3P)$ (6)
$O(^1D) + N_2 \rightarrow O(^3P)$ (7)
$OH + NO_2 + M \rightarrow HNO_3$ (8)

Clicker Q:

With increasing altitude O(^{1}D) mixing ratio in the troposphere should:

a) Decrease
b) Increase
c) No net effect
d) Increase then decrease
E) I don't know

The Many Faces of Atmospheric Ozone



In stratosphere: UV shield

In middle/upper troposphere: greenhouse gas

In lower/middle troposphere: precursor of OH, main atmospheric oxidant

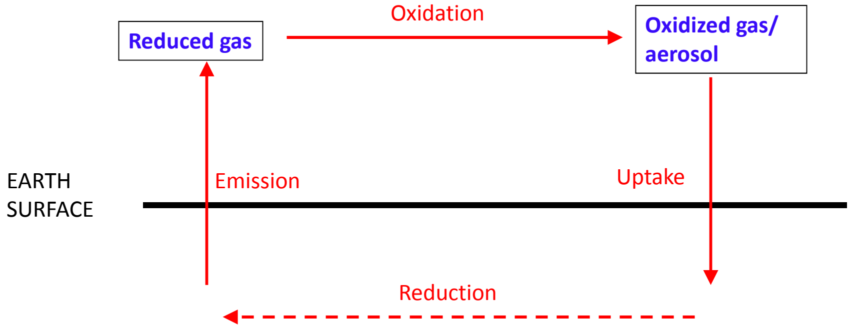
In surface air: toxic to humans and vegetation

From Jacob

The Atmosphere: Oxidizing Medium in Global Biogeochemical Cycles

Atmospheric oxidation is critical for removal of many pollutants, e.g.

- methane (major greenhouse gas)
- Toxic gases such as CO, benzene…
- Gases affecting the stratosphere such as HCFCs



From Jacob

The Troposphere was viewed as chemically inert until 1970

- *"The chemistry of the troposphere is mainly that of a large number of atmospheric constituents and of their reactions with molecular oxygen…Methane and CO are chemically quite inert in the troposphere"* [Cadle and Allen, Atmospheric Photochemistry, *Science*, 1970]
- Lifetime of CO estimated at 2.7 years (removal by soil) leads to concern about global CO pollution from increasing car emissions [Robbins and Robbins, Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants, *SRI report*, 1967]

FIRST BREAKTHROUGH:

- Measurements of cosmogenic ^{14}CO place a constraint of ~ 0.1 yr on the tropospheric lifetime of CO [Weinstock, *Science*, 1969]

SECOND BREAKTHROUGH:

- Tropospheric OH ~1×10^6 cm^{-3} predicted from $O(^1D)+H_2O$, results in tropospheric lifetimes of ~0.1 yr for CO and ~2 yr for CH_4 [Levy, *J. Geophys. Res.* 1973]

THIRD BREAKTHROUGH:

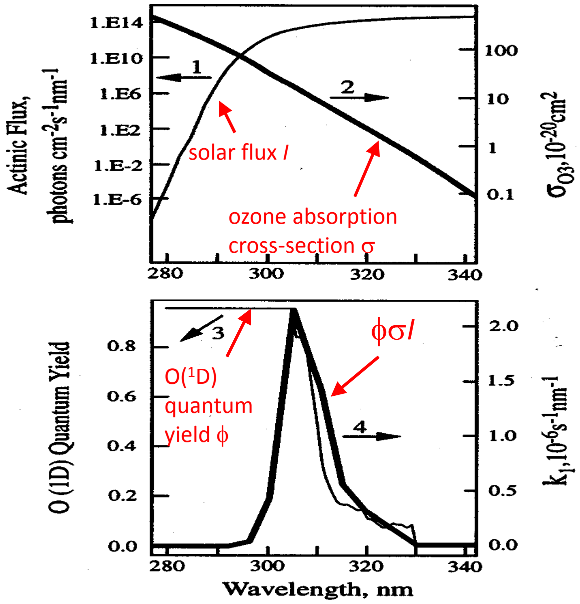
- Methylchloroform observations provide indirect evidence for OH at levels of $2\text{-}5\times10^5$ cm^{-3} [Singh, *Geophys. Res. Lett. 1977*]

…but direct measurements of tropospheric OH had to wait until the 1990s

From Jacob

Why was tropospheric OH difficult to figure out?

Production of O(^{1}D) in troposphere takes place in narrow band [290-320 nm]



From Jacob

Until ~1990, prevailing view was that tropospheric ozone originated mainly from stratosphere …but that cannot work.

- Estimate ozone flux F_{O3} across tropopause (strat-trop exchange)
  - Total O_3 col = 5x10^{13} moles
  - 10% of that is in troposphere
  - Res. time of air in strat = 1.4 yr

  } F_{O3} = 3x10^{13} moles yr^{-1}
- Estimate CH_4 source S_{CH4}:
  - Mean concentration = 1.7 ppmv
  - Lifetime = 9 years

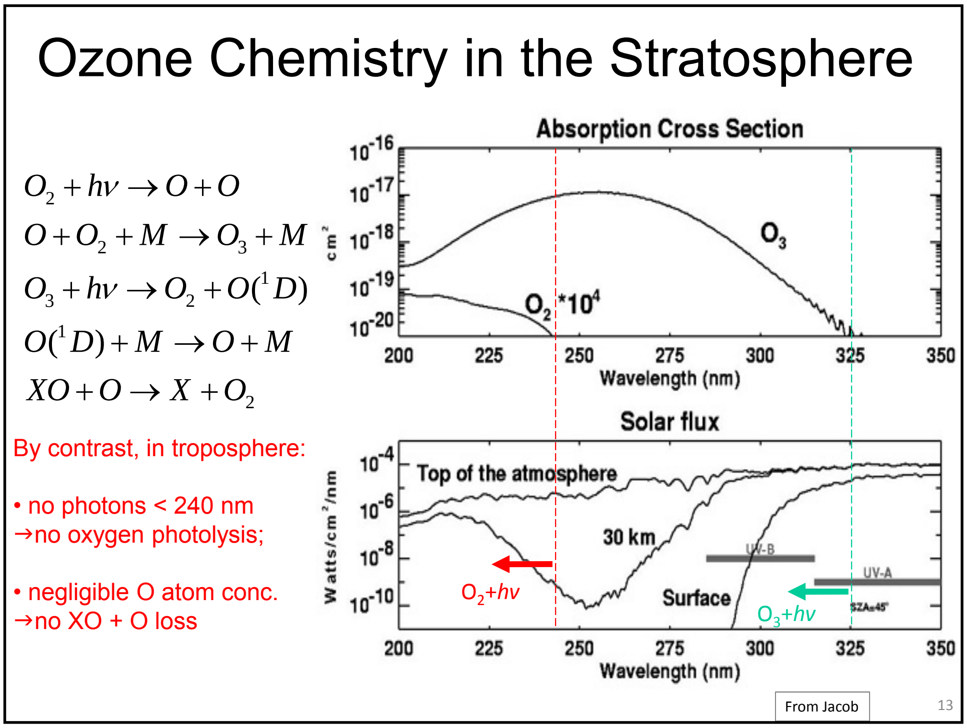
  } S_{CH4} = 3x10^{13} moles yr^{-1}
- Estimate CO source S_{CO}:
  - Mean concentration = 100 ppbv
  - Lifetime = 2 months

  } S_{CO} = 9.7x10^{13}moles yr^{-1}

$S_{CO}+ S_{CH4} > 2F_{O3}$ ⇨ OH would be titrated!

We need a much larger source of tropospheric ozone

From Jacob



Ozone Chemistry in the Stratosphere

$$O_2 + h\nu \rightarrow O + O$$

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

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

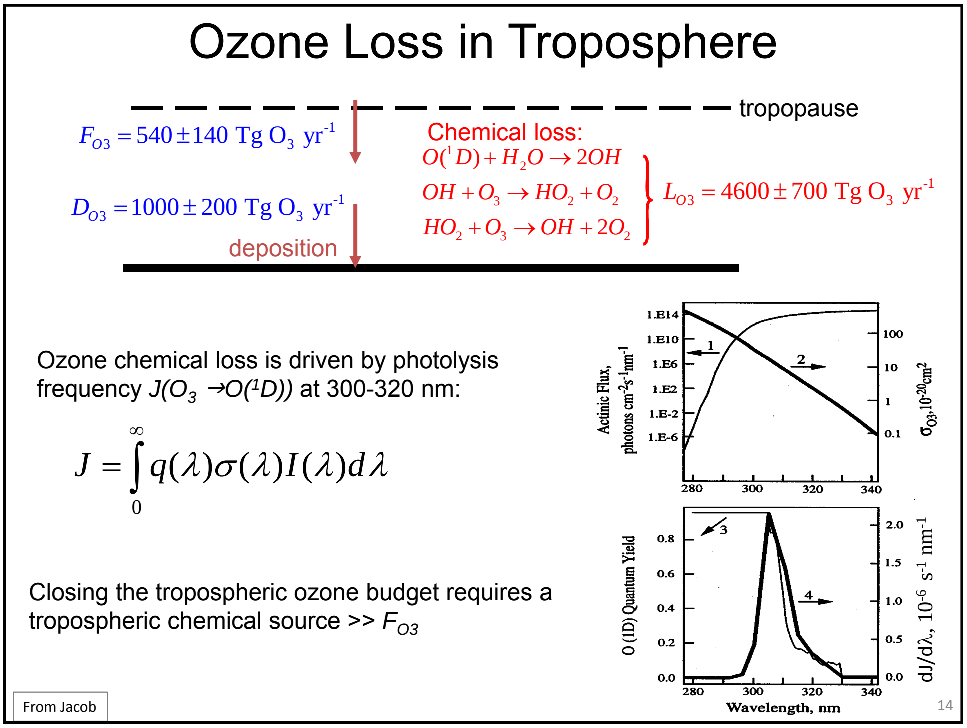
$$O(^1D) + M \rightarrow O + M$$

$$XO + O \rightarrow X + O_2$$

By contrast, in troposphere:

- no photons < 240 nm
→no oxygen photolysis;
- negligible O atom conc.
→no XO + O loss

From Jacob



Ozone Loss in Troposphere

$$F_{O3} = 540 \pm 140 \text{ Tg } O_3 \text{ yr}^{-1}$$

$$D_{O3} = 1000 \pm 200 \text{ Tg } O_3 \text{ yr}^{-1}$$

deposition

Chemical loss:

$$\left.\begin{array}{l} O(^1D) + H_2O \rightarrow 2OH \\ OH + O_3 \rightarrow HO_2 + O_2 \\ HO_2 + O_3 \rightarrow OH + 2O_2 \end{array}\right\} L_{O3} = 4600 \pm 700 \text{ Tg } O_3 \text{ yr}^{-1}$$

Ozone chemical loss is driven by photolysis frequency $J(O_3 \rightarrow O(^1D))$ at 300-320 nm:

$$J = \int_0^\infty q(\lambda)\sigma(\lambda)I(\lambda)d\lambda$$

Closing the tropospheric ozone budget requires a tropospheric chemical source >> F_{O3}

From Jacob

Stratospheric Ozone and Tropospheric OH

Clicker Q:

How would a thinning of the stratospheric ozone layer affect tropospheric OH concentrations?

a) Decrease
b) Increase
c) No net effect
d) Increase in regions and decrease in others
e) I don't know

Ozone Production in Troposphere: CO

Photochemical oxidation of CO catalyzed by hydrogen oxide radicals (HO_x) in the presence of nitrogen oxide radicals (NO_x)

HO_x = H + OH + HO_2 (+ RO + RO_2)
NO_x = NO + NO_2

Oxidation of CO:

$$CO + OH \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow OH + NO_2$$

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

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

$$\text{Net: } CO + 2O_2 \rightarrow CO_2 + O_3$$

*Note that neither NO_x nor HO_x are in the net reaction since they are acting as catalysts

Draw Schematic of CO oxidation with:

- **HO_x and NO_x family components should be cycles**
- **CO, CO_2, O_2, O_3 are not contained in cycles**

Ozone Production in Troposphere: CO + Radical Termination Reactions

CO oxidation:

Radical formation/propagation, ozone formation reactions:

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$\underline{O + O_2 + M \rightarrow O_3 + M}$$
$$\text{Net: } CO + 2O_2 \rightarrow CO_2 + O_3$$

Draw Schematic of CO oxidation now including radical termination reactions:

- **Represent HO_x and NO_x families both by a single enclosed box (e.g. no NO <=> NO_2 shown).**
- **Also add in arrows for HO_x net production rxns**

HO_x-NO_x Radical Termination steps:

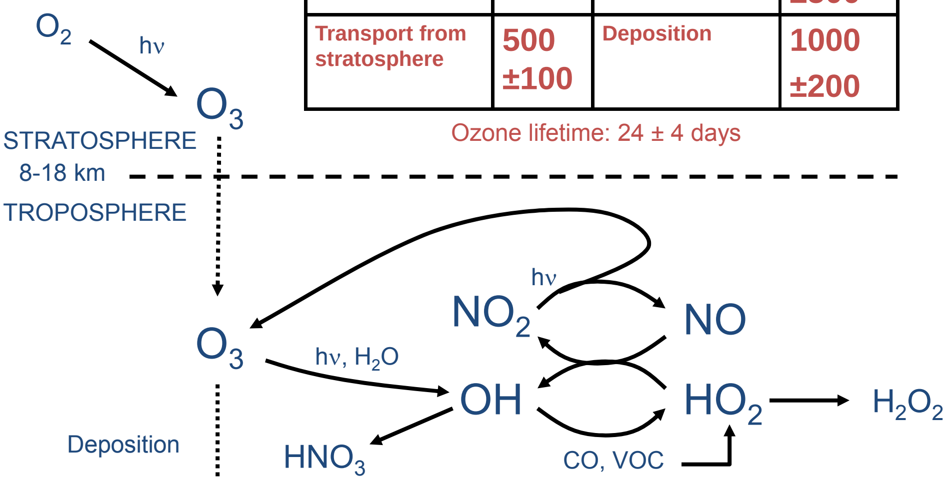
$$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$$
$$OH + NO_2 + M \rightarrow HNO_3 + M$$

Global Budget of Tropospheric Ozone (Tg O_3 yr^{-1})

IPCC (2007) average of 12 models

Chem prod in troposphere	**4700 ±700**	**Chem loss in troposphere**	**4200 ±500**
Transport from stratosphere	**500 ±100**	**Deposition**	**1000 ±200**

Ozone lifetime: 24 ± 4 days



From Jacob

Carbon Monoxide in Atmosphere

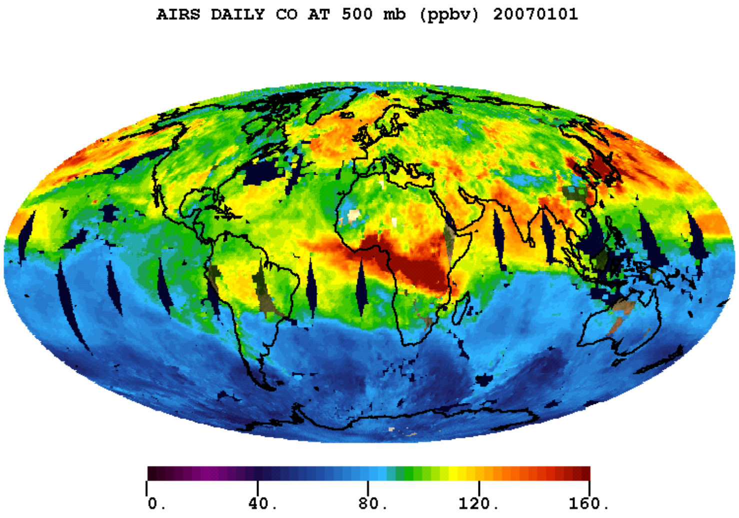
Source: incomplete combustion
Sink: oxidation by OH (lifetime of 2 months)

	Range of estimates (Tg CO yr $^{-1}$)
Sources	1800–2700
Fossil fuel combustion/industry	300–550
Biomass burning	300–700
Vegetation	60–160
Oceans	20–200
Oxidation of methane	400–1000
Oxidation of other hydrocarbons	200–600
Sinks	2100–3000
Tropospheric oxidation by OH	1400–2600
Stratosphere	~ 100
Soil uptake	250–640

From Jacob

Observations of CO from Space

(AIRS Satellite Instrument)

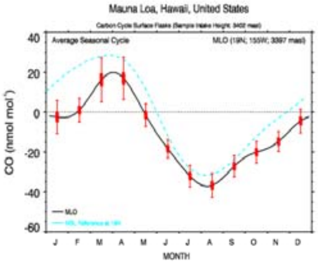


From Jacob

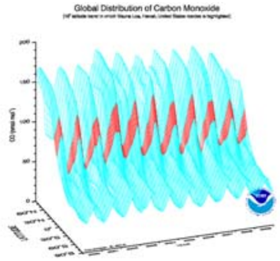
AIRS Satellite CO data at 500 hPa (W.W. McMillan)

Spatial and Seasonal Cycles of CO

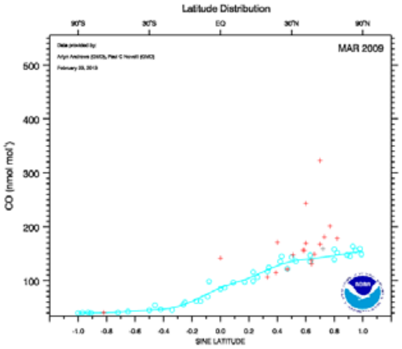
Seasonal Cycle at Mauna Loa, Hawaii:



Seasonal/Latitudinal Trends:



Latitudinal Trends (March 2009)



Seasonal Cycle of Latitudinal Global Background:

http://www.esrl.noaa.gov/gmd/dv/iadv/graph.php?code=MLO&program=ccgg&type=lg
(select gas from drop-down)

CO & OH in the Troposphere

Clicker Q:

If the source of CO were to double, CO concentrations would:

(assume that CO is the only sink of OH)

a) Double
b) More than double
c) Less than double
d) Stay the same
e) I don't know

CO Oxidation & O_3 Destruction vs. Production? NO_x!

Very Clean (very low NO_x)

$$CO + OH + M \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + O_3 \rightarrow OH + 2O_2$$

Net: $\boldsymbol{CO + O_3 \rightarrow CO_2 + O_2}$

Net Ozone Destruction

Polluted (with NO_x)

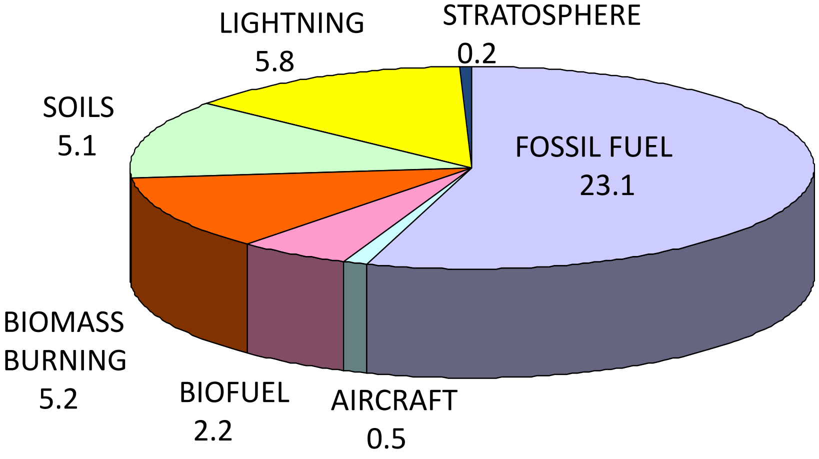
$$CO + OH + M \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + hv \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

Net: $\boldsymbol{CO + 2O_2 \rightarrow CO_2 + O_3}$

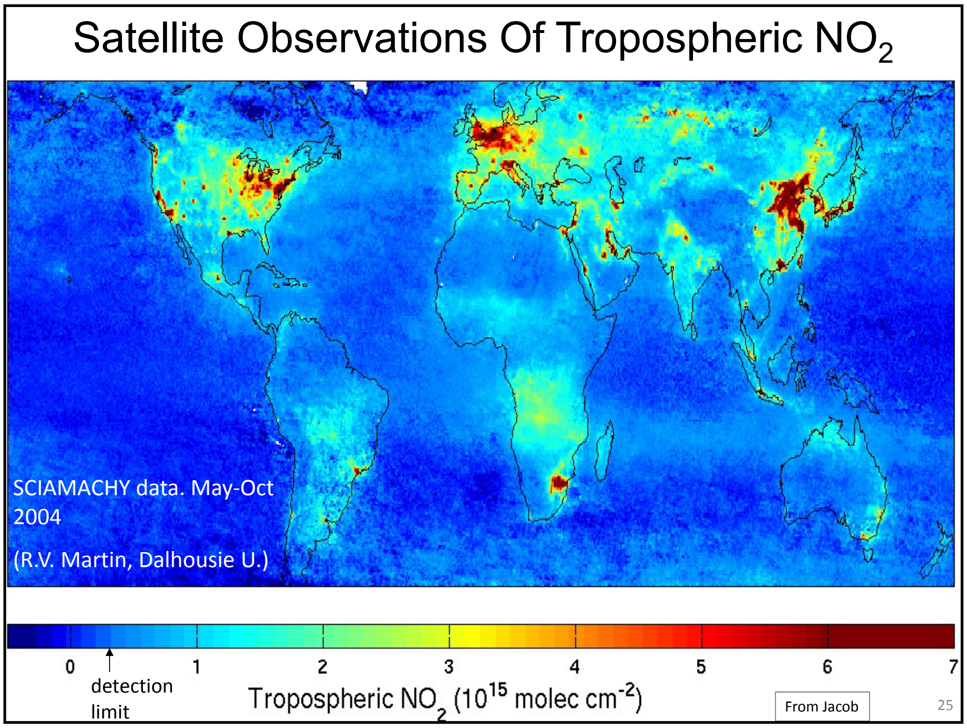
Net Ozone Production

Adapted from Tolbert

NO_x Emissions (Tg N yr^{-1}) to Troposphere



From Jacob

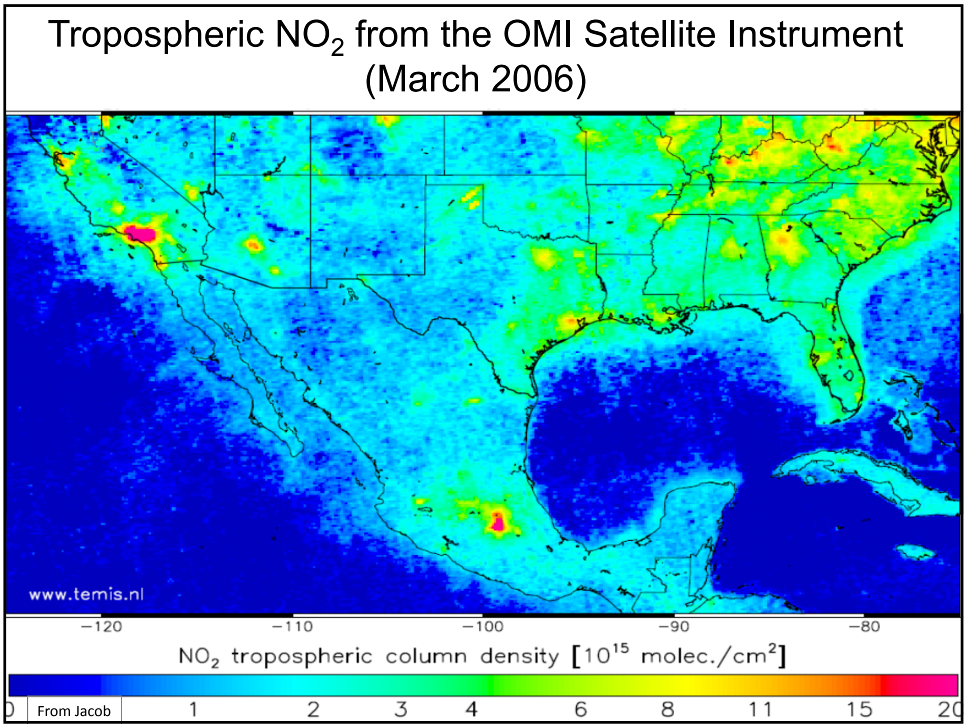


Satellite Observations Of Tropospheric NO_2

SCIAMACHY data. May-Oct 2004

(R.V. Martin, Dalhousie U.)

From Jacob

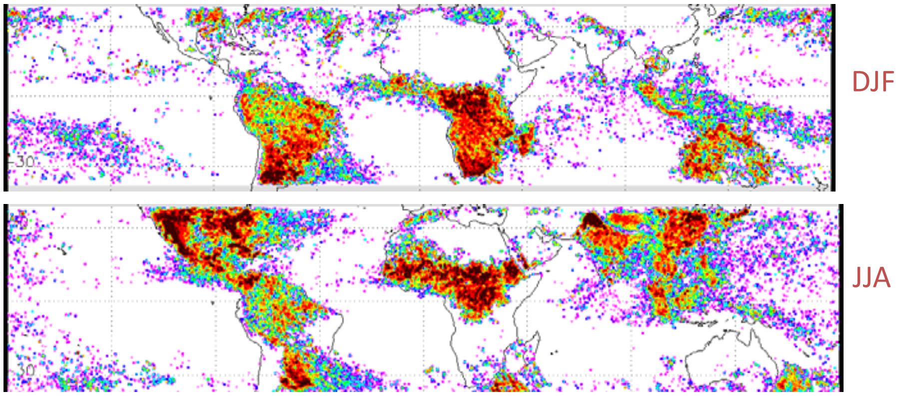


Tropospheric NO_2 from the OMI Satellite Instrument (March 2006)

www.temis.nl

From Jacob

Lightning flashes seen from space (2000)



From Jacob

NO_x in the Troposphere

Clicker Q:

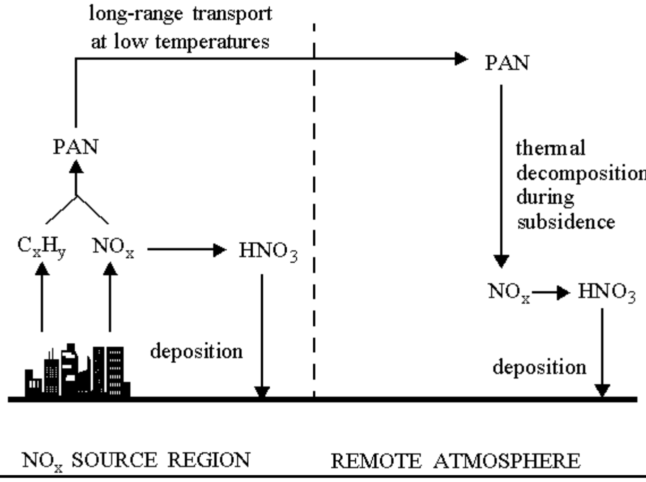
If the source of NO_x were to double, NO_x concentrations would:

a) Double
b) More than double
c) Less than double
d) Stay the same
e) I don't know

Peroxyacetylnitrate (PAN) as Reservoir for Long-range Transport of NO_x

$$CH_3C(O)O_2 + NO_2 + M \leftrightarrow CH_3C(O)O_2NO_2 + M$$

⟵Increasing Temperature



long-range transport at low temperatures

PAN

PAN

thermal decomposition during subsidence

C_xH_y NO_x → HNO_3

NO_x → HNO_3

deposition

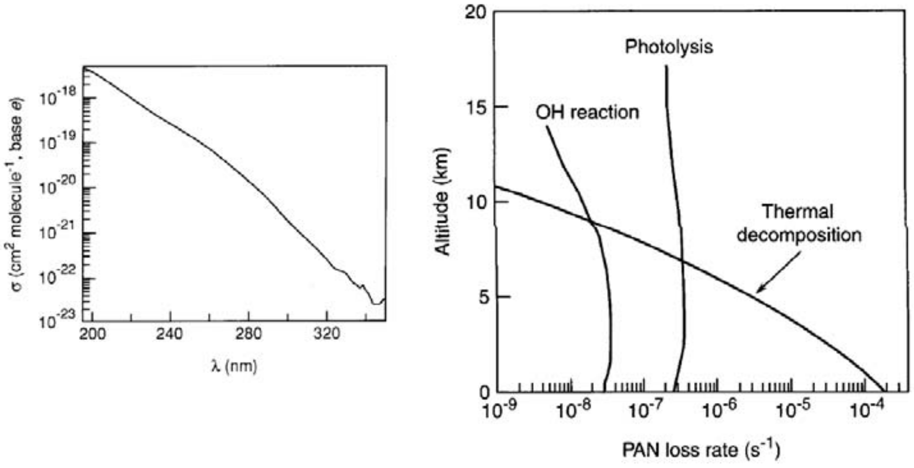
deposition

NO_x SOURCE REGION

REMOTE ATMOSPHERE

From Jacob

Can Photolysis Compete with Thermal Unimolecular Rxn?



Clicker Q:

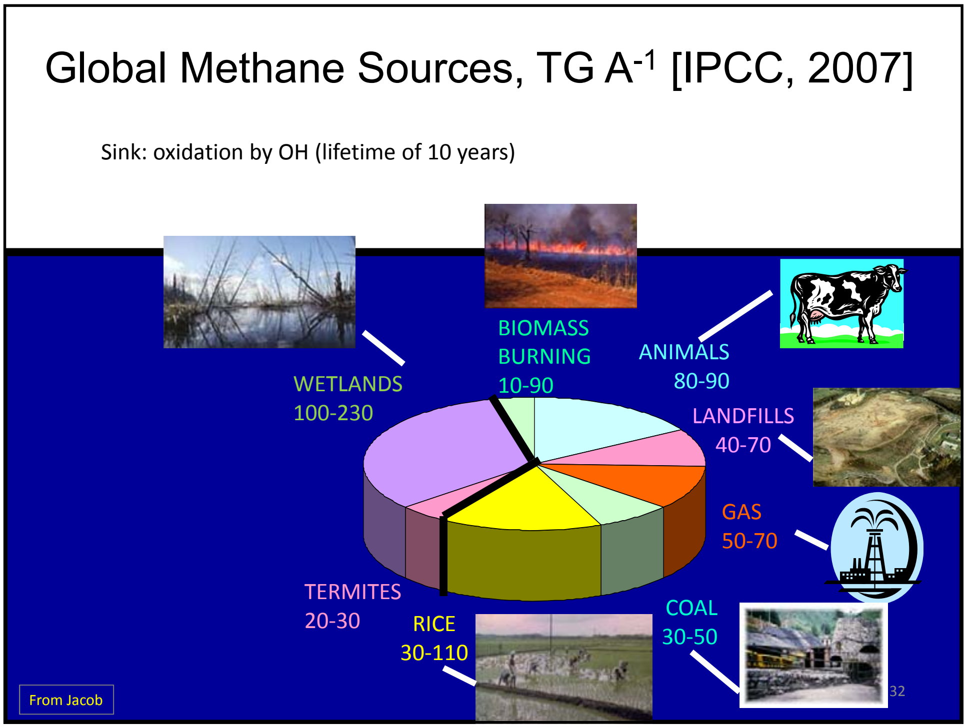
What is the lifetime of PAN at 10 km?

- a) 1 day
- b) 1 week
- c) 1 month
- d) 1 year
- e) I don't know

Adapted from Jacob

Fuels for O_3 Production

- ~~CO + NO_x~~
- Hydrocarbons (+ NO_x)
  - Methane (CH_4)
  - More complex hydrocarbons (non-methane HCs or VOCs)



Global Methane Sources, TG A^{-1} [IPCC, 2007]

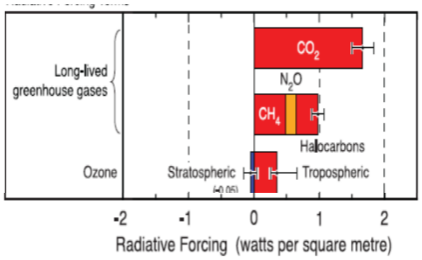
Sink: oxidation by OH (lifetime of 10 years)

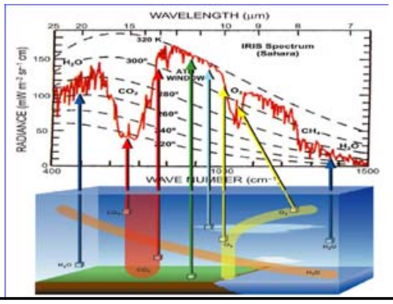
From Jacob

Methane: #2 Anthropogenic Greenhouse Gas

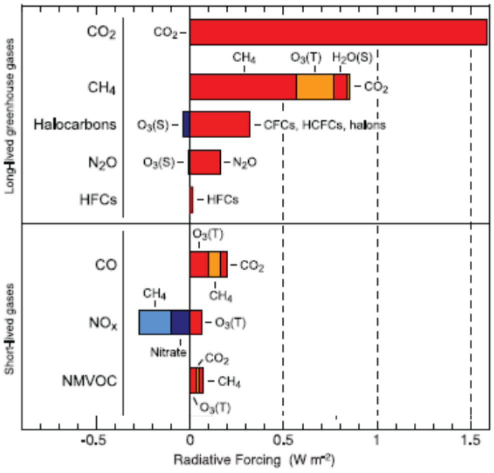
Greenhouse radiative forcing of climate between 1750 and 2005 [IPCC, 2007]

Referenced to concentration



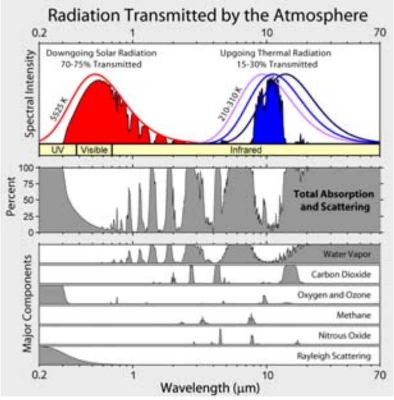


Referenced to emission

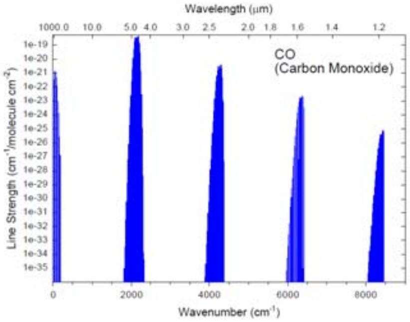


From Jacob

Carbon Monoxide and Climate?



http://en.wikipedia.org/wiki/File:Atmospheric_Transmission.png



http://www.coe.ou.edu/sserg/web/Results/results.htm

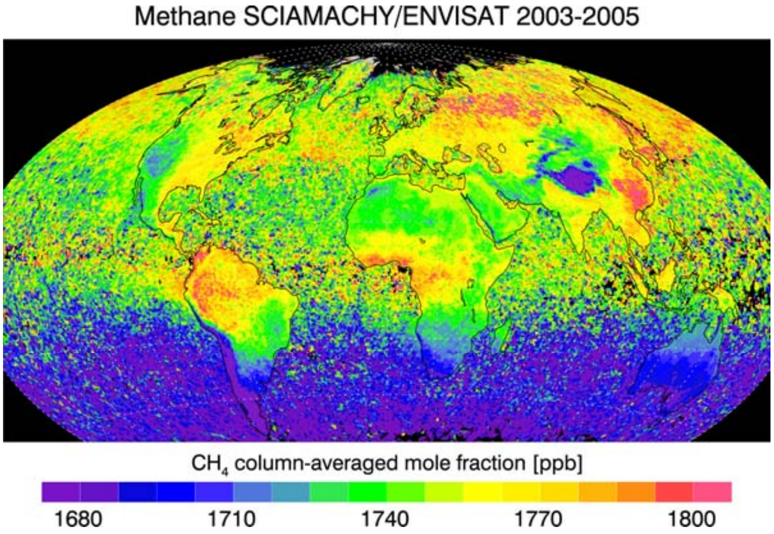
Clicker Q:

How does carbon monoxide (CO) affect Earth's radiative balance?

a) Directly
b) Indirectly
c) Both
d) Neither
e) I don't know

Measurement of Methane from Space

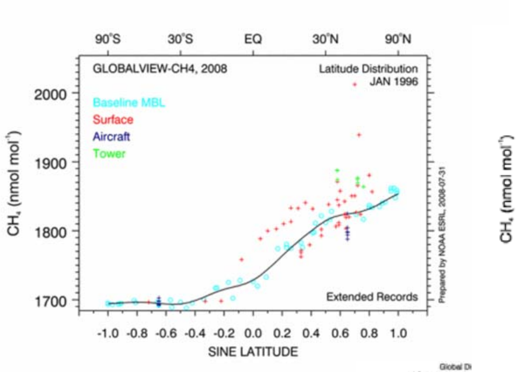
Detect solar backscatter in vibrational band at 2.265-2.280 µm

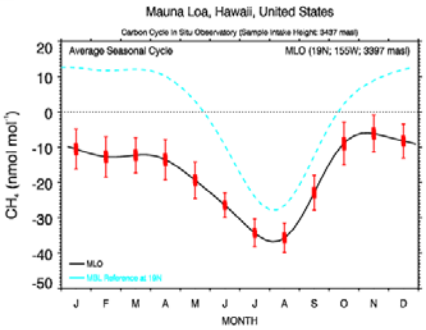


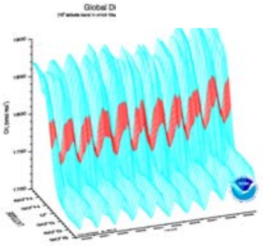
From Jacob

Global Distribution Of Methane

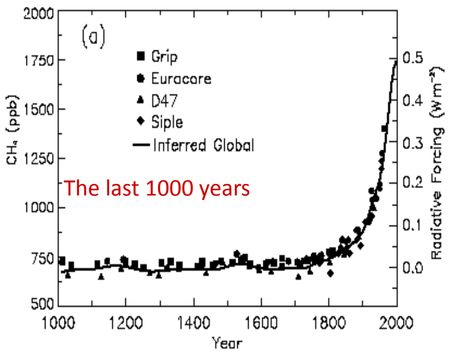
NOAA/GMD surface air measurements



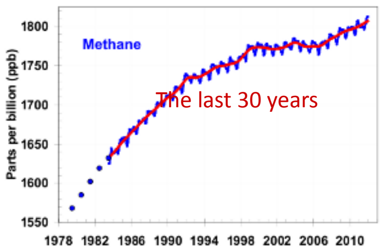




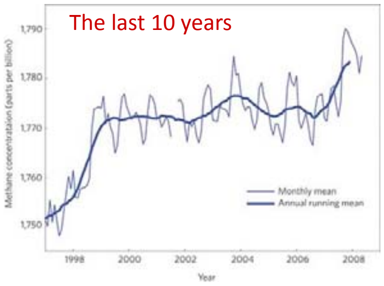
Historical Trends in Methane



The last 1000 years



The last 30 years



The last 10 years

Adapted from Jacob

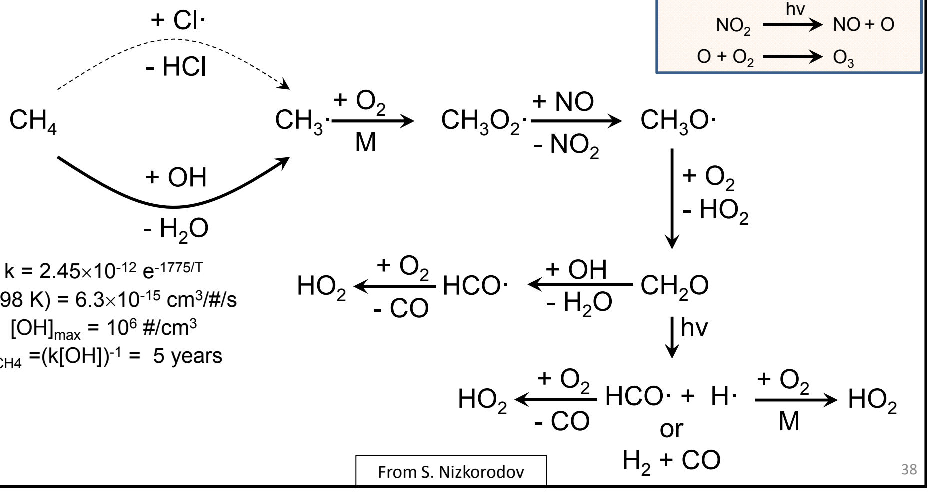
Oxidation of CH_4: High NO_x Case

$k = 1.1\times10^{-11}\ e^{-1440/T}$
$k(298\ K) = 1.0\times10^{-13}\ cm^3/\#/s$
$[Cl]_{max} = 10^4\ \#/cm^3$
$\tau_{CH4} = (k[Cl])^{-1} =$ 32 years

Net reaction if only HCO+H from CH_2O (+CO oxidation):

$$CH_4 + 10O_2 \rightarrow CO_2 + H_2O + 5O_3 + 2OH$$

$$NO + HO_2 \longrightarrow NO_2 + OH$$
$$NO_2 \xrightarrow{h\nu} NO + O$$
$$O + O_2 \longrightarrow O_3$$

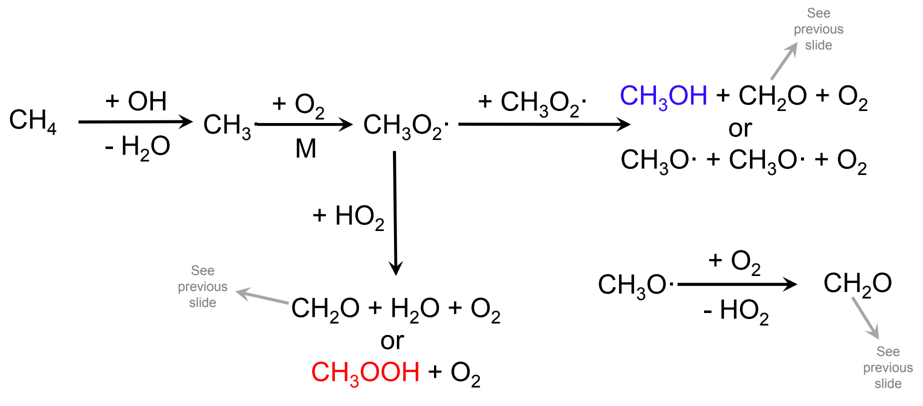


$$CH_4 \xrightarrow[-HCl]{+Cl\cdot} CH_3\cdot$$
$$CH_4 \xrightarrow[-H_2O]{+OH} CH_3\cdot \xrightarrow[M]{+O_2} CH_3O_2\cdot \xrightarrow[-NO_2]{+NO} CH_3O\cdot \xrightarrow[-HO_2]{+O_2} CH_2O$$
$$HO_2 \xleftarrow[-CO]{+O_2} HCO\cdot \xleftarrow[-H_2O]{+OH} CH_2O$$
$$CH_2O \xrightarrow{h\nu} HCO\cdot + H\cdot \text{ or } H_2 + CO$$
$$HO_2 \xleftarrow[-CO]{+O_2} HCO\cdot \qquad H\cdot \xrightarrow[M]{+O_2} HO_2$$

$k = 2.45\times10^{-12}\ e^{-1775/T}$
$k(298\ K) = 6.3\times10^{-15}\ cm^3/\#/s$
$[OH]_{max} = 10^6\ \#/cm^3$
$\tau_{CH4} = (k[OH])^{-1} =$ 5 years

From S. Nizkorodov

Oxidation of CH_4: Low NO_x Case



$CH_4 \xrightarrow[-H_2O]{+OH} CH_3 \xrightarrow[M]{+O_2} CH_3O_2\cdot \xrightarrow{+CH_3O_2\cdot}$ $CH_3OH + CH_2O + O_2$ or $CH_3O\cdot + CH_3O\cdot + O_2$

See previous slide

$CH_3O_2\cdot \xrightarrow{+HO_2}$ $CH_2O + H_2O + O_2$ or $CH_3OOH + O_2$

See previous slide

$CH_3O\cdot \xrightarrow[-HO_2]{+O_2} CH_2O$

See previous slide

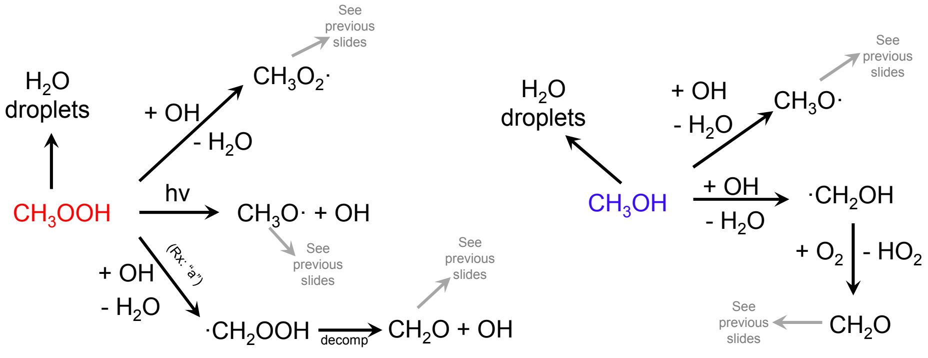
We already know what happens to CH_2O (it is converted to H_2, HO_2 and CO).

How about CH_3OOH and CH_3OH?
(see next slide)

Adapted from S. Nizkorodov

Oxidation of CH_3OOH and CH_3OH

(continuation of low-NO_x CH_4 oxidation)



H_2O droplets $\leftarrow CH_3OOH$

$CH_3OOH \xrightarrow[-H_2O]{+OH} CH_3O_2\cdot$ See previous slides

$CH_3OOH \xrightarrow{hv} CH_3O\cdot + OH$ See previous slides

$CH_3OOH \xrightarrow[-H_2O]{+OH}$ (Rx: "a") $\cdot CH_2OOH \xrightarrow[decomp]{} CH_2O + OH$ See previous slides

H_2O droplets $\leftarrow CH_3OH$

$CH_3OH \xrightarrow[-H_2O]{+OH} CH_3O\cdot$ See previous slides

$CH_3OH \xrightarrow[-H_2O]{+OH} \cdot CH_2OH \xrightarrow[-HO_2]{+O_2} CH_2O$ See previous slides

Net reaction of CH_4 oxidation in low-NO_x assuming:
a) CH_3OOH reacts only by reaction pathway "a"
b) CH_2O reacts only with OH (no photolysis; see last slides)

Net: $CH_4 + 3OH + 2O_2 \rightarrow CO_2 + 3H_2O + HO_2$

Recall high-NO_x net reaction:
$CH_4 + 10O_2 \rightarrow CO_2 + H_2O + 5O_3 + 2OH$

Adapted rom S. Nizkorodov

Tropospheric Oxidation & Ozone Formation II

<u>Required</u> Reading: Jacob Chapters 11 & 12

Atmospheric Chemistry
ATOC-5151 / CHEM 5151
Prof. Jose-Luis Jimenez
Spring 2013
Lecture by Doug Day

Thermodynamics of CO Oxidation

CO oxidation rxns:

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

Net: $CO + 2O_2 \rightarrow CO_2 + O_3$

Clicker Q:

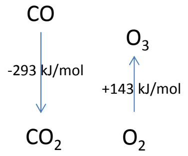
Is the calculation that 49% of the chemical energy given by CO combustion to CO_2 is stored in the formation of O_3?

a) Correct
b) Incorrect
c) Approximately
d) Not possible without further details.
e) I don't know

Enthalpy of formation (at 298 K, 1 Atm)

Compound	$\Delta_f H^o$(kJ mol^{-1})
CO	-111
O_2	0
CO_2	-394
O_3	143

CO (+0.5O_2)→ CO_2: $\Delta_f H^o$ = -394 – (-111+0) = -293 kJ/mol
1.5O_2 → O_3: $\Delta_f H^o$ = +143 – 0 = +143 kJ/mol



Efficiency?:
143/293 = 0.49 => 49%

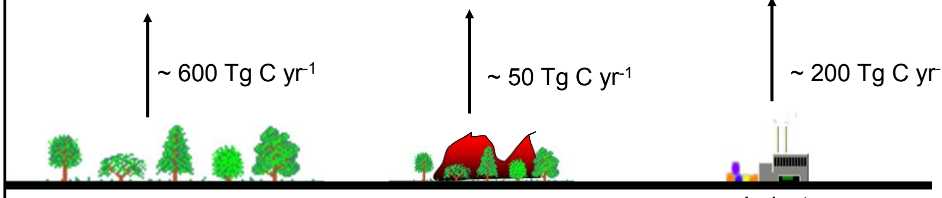
CH_4, NO_x, O_3 in the Troposphere

Clicker Q:

Additional sources of NO_x in remote regions should result in blank in O_3 production from CH_4 oxidation.

a) a decrease
b) catalytic destruction
c) an increase
d) no change
e) I don't know

Non-methane VOC Emissions



Isoprene, terpenes, oxygenates… ~ 600 Tg C yr^{-1} Vegetation

Alkenes, aromatics, oxygenates… ~ 50 Tg C yr^{-1} Biomass burning

Alkanes, alkenes, aromatics… ~ 200 Tg C yr^{-1} Industry Transportation

Largest global flux is from isoprene (300-500 Tg C yr^{-1})

From Jacob

Lifetimes of Organics

- As always: enormous number of possibilities, *but what is important?*

Org + X → Products (X is an oxidant)

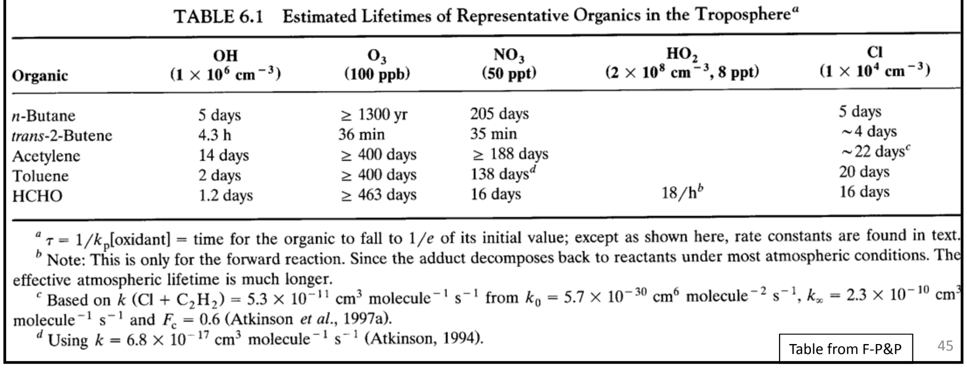


TABLE 6.1 Estimated Lifetimes of Representative Organics in the Troposphere[a]

Organic	OH (1×10^6 cm^{-3})	O_3 (100 ppb)	NO_3 (50 ppt)	HO_2 (2×10^8 cm^{-3}, 8 ppt)	Cl (1×10^4 cm^{-3})
n-Butane	5 days	≥ 1300 yr	205 days		5 days
trans-2-Butene	4.3 h	36 min	35 min		~4 days
Acetylene	14 days	≥ 400 days	≥ 188 days		~22 days[c]
Toluene	2 days	≥ 400 days	138 days[d]		20 days
HCHO	1.2 days	≥ 463 days	16 days	18/h[b]	16 days

[a] $\tau = 1/k_p$[oxidant] = time for the organic to fall to $1/e$ of its initial value; except as shown here, rate constants are found in text.

[b] Note: This is only for the forward reaction. Since the adduct decomposes back to reactants under most atmospheric conditions. The effective atmospheric lifetime is much longer.

[c] Based on k (Cl + C_2H_2) = 5.3×10^{-11} cm^3 molecule^{-1} s^{-1} from $k_0 = 5.7 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1}, $k_\infty = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $F_c = 0.6$ (Atkinson *et al.*, 1997a).

[d] Using $k = 6.8 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1994).

Table from F-P&P

Alkanes + OH·

- OH· has strong tendency to abstract H

  RH + OH· → R· + H_2O
  - We will focus on R· soon
- Rate increases with size and complexity
  - Maximum rate?
- CH_4 is far slower than others
  - Focus on Non-Methane Hydrocarbons (NMHC) for urban smog
  - Why CH_4 survives and builds up to be a greenhouse gas

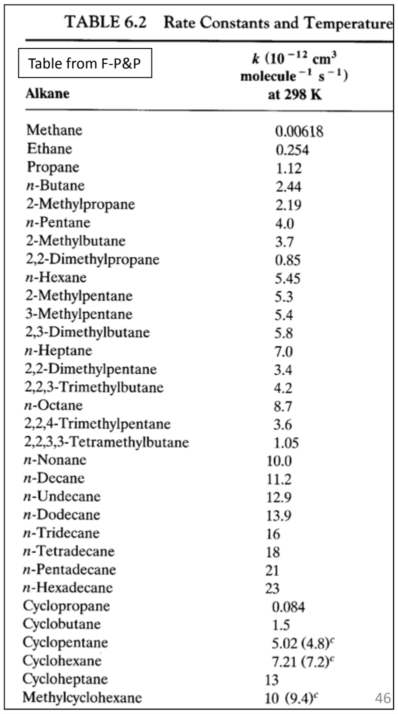


TABLE 6.2 Rate Constants and Temperature

Table from F-P&P

Alkane	k (10^{-12} cm^3 molecule^{-1} s^{-1}) at 298 K
Methane	0.00618
Ethane	0.254
Propane	1.12
n-Butane	2.44
2-Methylpropane	2.19
n-Pentane	4.0
2-Methylbutane	3.7
2,2-Dimethylpropane	0.85
n-Hexane	5.45
2-Methylpentane	5.3
3-Methylpentane	5.4
2,3-Dimethylbutane	5.8
n-Heptane	7.0
2,2-Dimethylpentane	3.4
2,2,3-Trimethylbutane	4.2
n-Octane	8.7
2,2,4-Trimethylpentane	3.6
2,2,3,3-Tetramethylbutane	1.05
n-Nonane	10.0
n-Decane	11.2
n-Undecane	12.9
n-Dodecane	13.9
n-Tridecane	16
n-Tetradecane	18
n-Pentadecane	21
n-Hexadecane	23
Cyclopropane	0.084
Cyclobutane	1.5
Cyclopentane	5.02 (4.8)[c]
Cyclohexane	7.21 (7.2)[c]
Cycloheptane	13
Methylcyclohexane	10 (9.4)[c]

Alkanes + Cl·

- Cl· also likes to abstract H

  RH + Cl· → R· + HCl
- Also forms an alkyl radical
- Reactions compared with collision rate?
- Importance vs. OH chemistry?

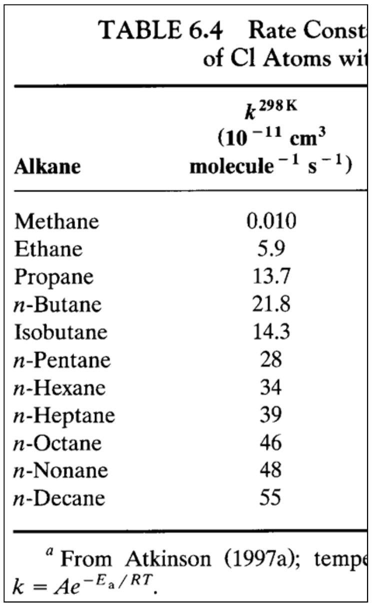


TABLE 6.4 Rate Const
of Cl Atoms wi

Alkane	**$k^{298 K}$ (10^{-11} cm^3 molecule^{-1} s^{-1})**
Methane	0.010
Ethane	5.9
Propane	13.7
n-Butane	21.8
Isobutane	14.3
n-Pentane	28
n-Hexane	34
n-Heptane	39
n-Octane	46
n-Nonane	48
n-Decane	55

[a] From Atkinson (1997a); tempe
$k = Ae^{-E_a/RT}$.

Table from F-P&P

Fates of Alkyl Radicals (R·)

- Radical nomenclature:
  - Alkyl: R·
  - Alkylperoxide: R-O-O· or RO_2·
  - Alkoxy: R-O· or RO·
- R· from oxidation of alkanes
  - Generated with all oxidants
  - Fate is similar for H-abstraction radicals from other organics
- Only fate is reaction with O_2

  R· + O_2 + M → RO_2· + M
- k ~ 1 x 10^{-11} cm^3 molec^{-1} s^{-1}
  - Lifetime of R· at ground level?

Alkylperoxy Radicals ($RO_2\cdot$) I

- React mainly with NO, $HO_2\cdot$, $RO_2\cdot$, and NO_3
- $RO_2\cdot + NO \rightarrow$
  - Fast: k ~ 8×10^{-12} cm^3 $molec^{-1}$ s^{-1}
  - Do not vary much with R
  - Products
    - Mainly $\rightarrow RO\cdot + NO_2$
      - Again: this is how we make O_3 in the troposphere
    - Also $\rightarrow RONO_2$ (alkyl nitrate)
      - Yields increase with $RO_2\cdot$ size
- $CH_3O_2\cdot + NO_3\cdot \rightarrow CH_3O\cdot + NO_2 + O_2$
  - Fast k ~ 2×10^{-12}, important @ night

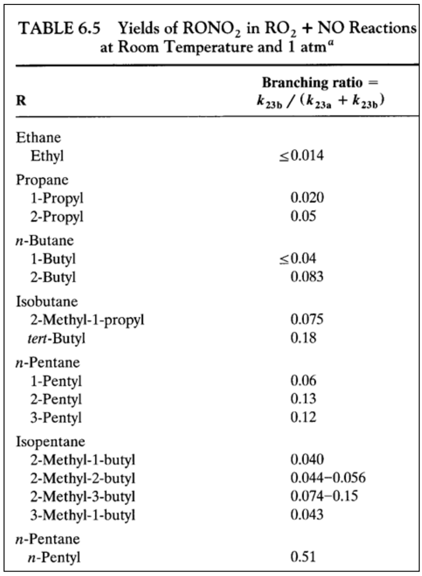


TABLE 6.5 Yields of $RONO_2$ in RO_2 + NO Reactions at Room Temperature and 1 atm[a]

R	Branching ratio = $k_{23b} / (k_{23a} + k_{23b})$
Ethane	
Ethyl	≤0.014
Propane	
1-Propyl	0.020
2-Propyl	0.05
n-Butane	
1-Butyl	≤0.04
2-Butyl	0.083
Isobutane	
2-Methyl-1-propyl	0.075
tert-Butyl	0.18
n-Pentane	
1-Pentyl	0.06
2-Pentyl	0.13
3-Pentyl	0.12
Isopentane	
2-Methyl-1-butyl	0.040
2-Methyl-2-butyl	0.044–0.056
2-Methyl-3-butyl	0.074–0.15
3-Methyl-1-butyl	0.043
n-Pentane	
n-Pentyl	0.51

Table from F-P&P

Alkylperoxy Radicals ($RO_2\cdot$) II

- $RO_2\cdot + HO_2\cdot \rightarrow ROOH + O_2$ (24a)

  $\rightarrow$ Carbonyl + $H_2O + O_2$ (24b)

  $\rightarrow ROH + O_3$ (24c)
  - ROOH is hydroperoxide R-O-O-H
  - Mostly by (24a) for small R, other channels contribute for larger R
  - k ~ 6×10^{-12} cm^3 $molec^{-1}$ s^{-1} @ room T
- $RO_2\cdot + RO_2\cdot \rightarrow 2RO\cdot + O_2$ (25a)

  $\rightarrow ROH + RCHO + O_2$ (25b)

  $\rightarrow ROOR + O_2$ (25c)

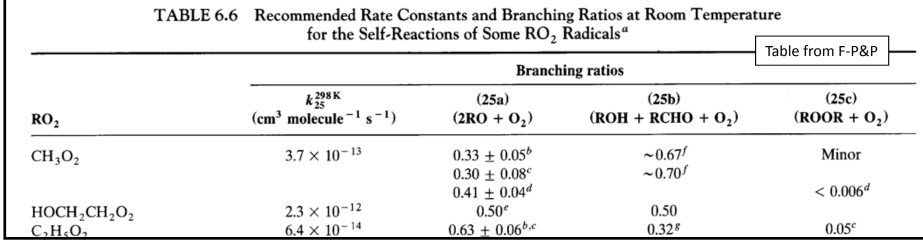


TABLE 6.6 Recommended Rate Constants and Branching Ratios at Room Temperature for the Self-Reactions of Some RO_2 Radicals[a]

Table from F-P&P

		Branching ratios		
RO_2	k_{25}^{298K} (cm^3 $molecule^{-1}$ s^{-1})	(25a) ($2RO + O_2$)	(25b) ($ROH + RCHO + O_2$)	(25c) ($ROOR + O_2$)
CH_3O_2	3.7×10^{-13}	0.33 ± 0.05[b] 0.30 ± 0.08[c] 0.41 ± 0.04[d]	~0.67[f] ~0.70[f]	Minor < 0.006[d]
$HOCH_2CH_2O_2$	2.3×10^{-12}	0.50[e]	0.50	
$C_2H_5O_2$	6.4×10^{-14}	0.63 ± 0.06[b,c]	0.32[g]	0.05[c]

Relative Importance of $RO_2\cdot$ Reactions

$$\text{Products} \xleftarrow[+\,HO_2\cdot]{+\,RO_2\cdot} RO_2\cdot \xrightarrow[-\,NO_2]{+\,NO} RO\cdot$$

Critical parameter is the ratio of the corresponding reaction rates:

$k\ (CH_3O_2 + NO) \approx 7.7\times10^{-12}\ \text{cm}^3\ \text{molec}^{-1}\ \text{s}^{-1}$ @ 298 K
$k\ (CH_3O_2 + HO_2) \approx 5.6\times10^{-13}\ \text{cm}^3\ \text{molec}^{-1}\ \text{s}^{-1}$ @ 298 K
$k\ (CH_3O_2 + CH_3O_2) \approx 4.7\times10^{-13}\ \text{cm}^3\ \text{molec}^{-1}\ \text{s}^{-1}$ @ 298 K

$[NO]_{urban} \approx 20\ \text{ppb} = 5\times10^{11}\ \text{molec cm}^{-3}$
$[HO_2]_{urban} \approx [CH_3O_2]_{urban} \approx 40\ \text{ppt} = 10^{9}\ \text{molec cm}^{-3}$
$\{\text{Rate}(CH_3O_2 + NO) / \text{Rates}(RO_2 + CH_3O_2)\}_{urban} \approx 4000$

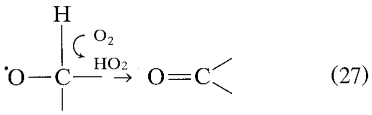
$[NO]_{clean} \approx 1\ \text{ppt} \approx 2\times10^{7}\ \text{molec cm}^{-3}$
$[HO_2]_{clean} \approx [CH_3O_2]_{clean} \approx 5\ \text{ppt} \approx 10^{8}\ \text{molec cm}^{-3}$
$\{\text{Rate}(CH_3O_2 + NO) / \text{Rates}(RO_2 + CH_3O_2)\}_{clean} \approx 1$

From S. Nizkorodov

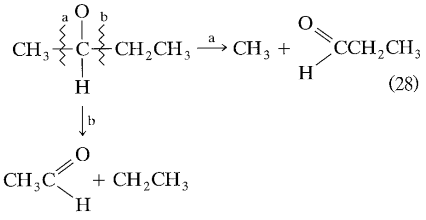
Conclusion: In urban atmosphere, reaction with NO dominates ("high NO_x limit"). In remote troposphere, both pathways are similar.

Alkoxy Radicals (RO·)

- *Three main fates*

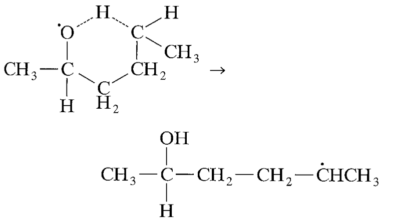


(27)



(28)

- Intramolecular



(29)

- Where isomerization is possible, it dominates
  - as R size increases
- Otherwise RO· + O_2

Schemes from F-P&P

Summary of Alkane Oxidation

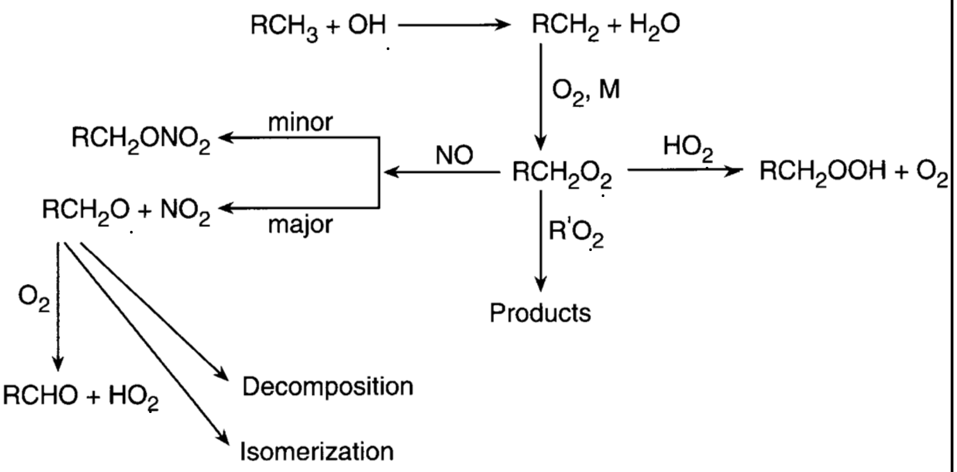


FIGURE 6.2 Summary of alkane oxidation by OH in air.

- *"Chemistry is all about electrons"*
- Species with unpaired electrons (radical) doing most of the work

Schemes from F-P&P

Alkenes + OH

- Remember that collision rate ~2.5 x 10^{-10}
- Very fast reactions, faster for larger alkenes
- Pressure dep., negative T dep.
  - Suports importance of addition to double b.
- Compare OH +
  - Propane: 1 x 10^{-12}
  - Propene: 26 x 10^{-12}
  - Heptane: 7 x 10^{-12}
  - Heptene: 40 x 10^{-12}

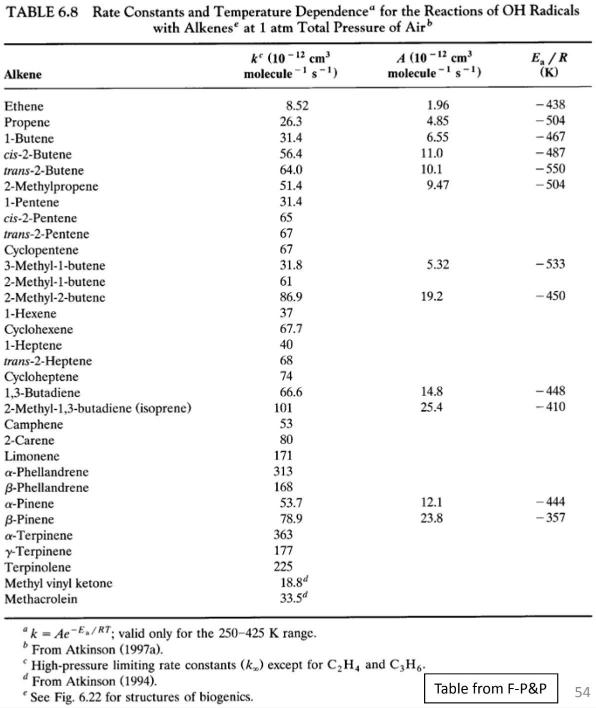


TABLE 6.8 Rate Constants and Temperature Dependence[a] for the Reactions of OH Radicals with Alkenes[e] at 1 atm Total Pressure of Air[b]

Alkene	k^c (10^{-12} cm^3 molecule^{-1} s^{-1})	A (10^{-12} cm^3 molecule^{-1} s^{-1})	E_a/R (K)
Ethene	8.52	1.96	−438
Propene	26.3	4.85	−504
1-Butene	31.4	6.55	−467
cis-2-Butene	56.4	11.0	−487
trans-2-Butene	64.0	10.1	−550
2-Methylpropene	51.4	9.47	−504
1-Pentene	31.4		
cis-2-Pentene	65		
trans-2-Pentene	67		
Cyclopentene	67		
3-Methyl-1-butene	31.8	5.32	−533
2-Methyl-1-butene	61		
2-Methyl-2-butene	86.9	19.2	−450
1-Hexene	37		
Cyclohexene	67.7		
1-Heptene	40		
trans-2-Heptene	68		
Cycloheptene	74		
1,3-Butadiene	66.6	14.8	−448
2-Methyl-1,3-butadiene (isoprene)	101	25.4	−410
Camphene	53		
2-Carene	80		
Limonene	171		
α-Phellandrene	313		
β-Phellandrene	168		
α-Pinene	53.7	12.1	−444
β-Pinene	78.9	23.8	−357
α-Terpinene	363		
γ-Terpinene	177		
Terpinolene	225		
Methyl vinyl ketone	18.8[d]		
Methacrolein	33.5[d]		

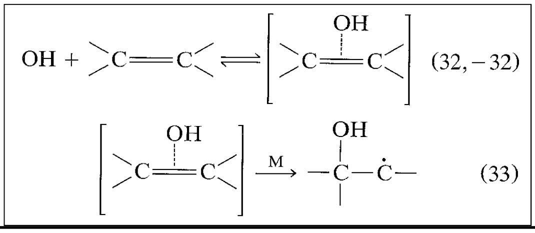
---

[a] $k = Ae^{-E_a/RT}$; valid only for the 250–425 K range.
[b] From Atkinson (1997a).
[c] High-pressure limiting rate constants (k_∞) except for C_2H_4 and C_3H_6.
[d] From Atkinson (1994).
[e] See Fig. 6.22 for structures of biogenics.

Table from F-P&P

Reactions of Alkenes

- E.g. HC_3-CH=CH-CH_3, 2-butene
- Double bond adds reactivity
  - For alkanes OH could abstract any H
    - No strong preference for reaction site
  - The double bond has extra electron density
    - Attacked by electrophilic radicals: OH, O_3, NO_3, Cl
    - "The double bond gets the whole molecule in trouble"
  - Alkenes "are more reactive" than alkanes



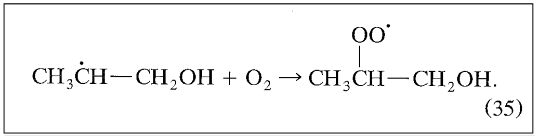
Schemes from F-P&P

What happens after OH addition?

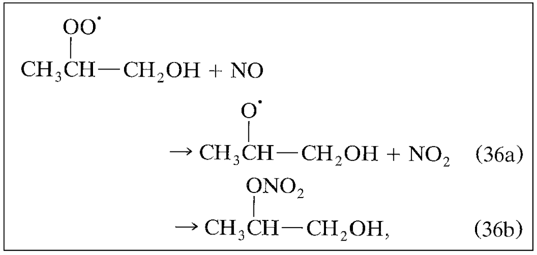
- → Hydroxy group + alkyl radical
- Alkyl radical → Peroxy radical
- Peroxy radical → Alkoxy radical or (stable) nitrate
- Alkoxy radical → reaction with O_2, decomposition, isomerization

$$\mathrm{OH + CH_3CH{=}CH_2 \rightarrow CH_3\dot{C}H{-}CH_2OH,} \quad (34a)$$

$$\rightarrow \mathrm{CH_3CH(OH){-}\dot{C}H_2.} \quad (34b)$$



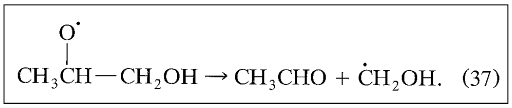
$$\mathrm{CH_3\dot{C}H{-}CH_2OH + O_2 \rightarrow CH_3\overset{\overset{OO^{\bullet}}{|}}{C}H{-}CH_2OH.} \quad (35)$$



$$\mathrm{CH_3\overset{\overset{OO^{\bullet}}{|}}{C}H{-}CH_2OH + NO}$$

$$\rightarrow \mathrm{CH_3\overset{\overset{O^{\bullet}}{|}}{C}H{-}CH_2OH + NO_2} \quad (36a)$$

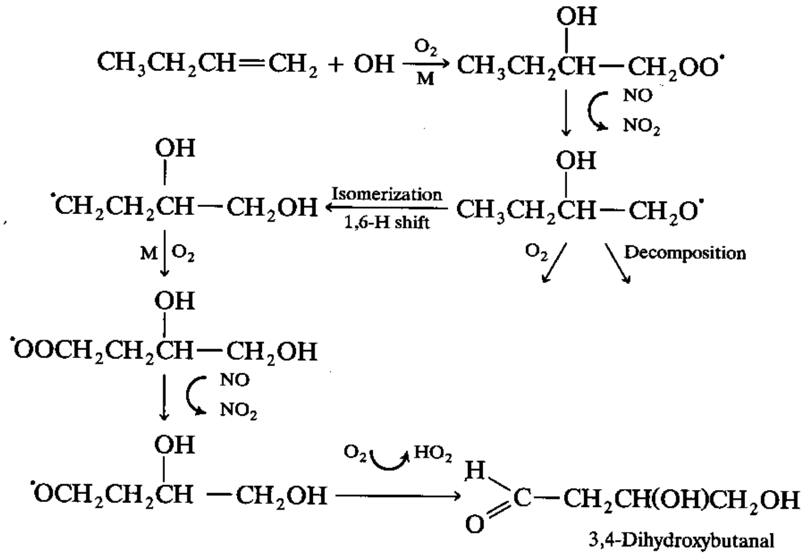
$$\rightarrow \mathrm{CH_3\overset{\overset{ONO_2}{|}}{C}H{-}CH_2OH,} \quad (36b)$$



$$\mathrm{CH_3\overset{\overset{O^{\bullet}}{|}}{C}H{-}CH_2OH \rightarrow CH_3CHO + \dot{C}H_2OH.} \quad (37)$$

Example of β-hydroxyalkyl Isomerization

- As for alkanes, larger alkoxy radicals isomerize:



O_3 + Alkenes

- Remember that collision rate ~2.5 x 10^{-10}
- Much slower reactions than for OH
- Compare
  - OH + Propene: 2.6 x 10^{-11}
  - O_3 + Propene: 1 x 10^{-17}
- But remember:
  - d[Org]/dt = - k[Oxidant][Org]
  - OH: 0.1 ppt
  - O_3: 100 ppb

So although ozonolysis of alkenes is a slow process, it is important in the atmosphere because of the large concentrations of O_3.

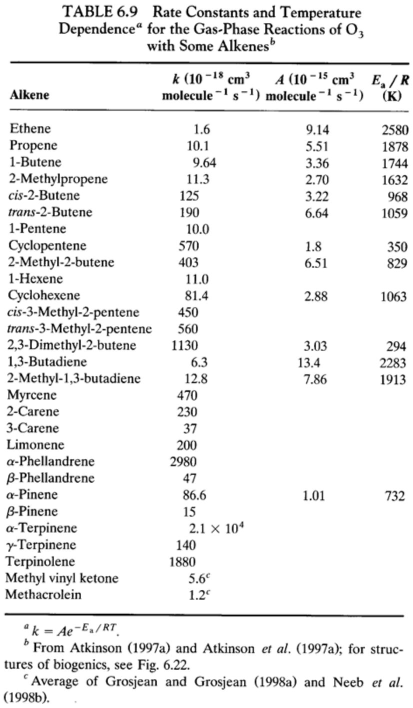


TABLE 6.9 Rate Constants and Temperature Dependence[a] for the Gas-Phase Reactions of O_3 with Some Alkenes[b]

Alkene	k (10^{-18} cm^3 molecule^{-1} s^{-1})	A (10^{-15} cm^3 molecule^{-1} s^{-1})	E_a/R (K)
Ethene	1.6	9.14	2580
Propene	10.1	5.51	1878
1-Butene	9.64	3.36	1744
2-Methylpropene	11.3	2.70	1632
cis-2-Butene	125	3.22	968
trans-2-Butene	190	6.64	1059
1-Pentene	10.0		
Cyclopentene	570	1.8	350
2-Methyl-2-butene	403	6.51	829
1-Hexene	11.0		
Cyclohexene	81.4	2.88	1063
cis-3-Methyl-2-pentene	450		
trans-3-Methyl-2-pentene	560		
2,3-Dimethyl-2-butene	1130	3.03	294
1,3-Butadiene	6.3	13.4	2283
2-Methyl-1,3-butadiene	12.8	7.86	1913
Myrcene	470		
2-Carene	230		
3-Carene	37		
Limonene	200		
α-Phellandrene	2980		
β-Phellandrene	47		
α-Pinene	86.6	1.01	732
β-Pinene	15		
α-Terpinene	2.1×10^4		
γ-Terpinene	140		
Terpinolene	1880		
Methyl vinyl ketone	5.6[c]		
Methacrolein	1.2[c]		

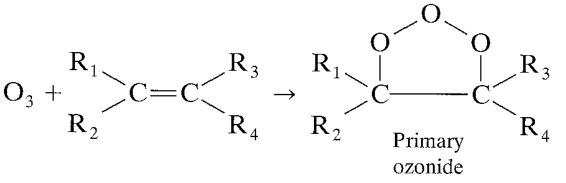
[a] $k = Ae^{-E_a/RT}$.

[b] From Atkinson (1997a) and Atkinson *et al.* (1997a); for structures of biogenics, see Fig. 6.22.

[c] Average of Grosjean and Grosjean (1998a) and Neeb *et al.* (1998b).

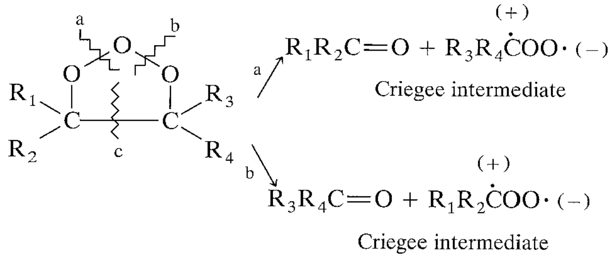
Mechanism of O_3 + Alkenes: First steps

- O_3 adds across the double bond



(42)

- The primary ozonide is not stable and breaks



c breaks, a or b break

(43)

Fate of Excited Criegee Intermediates

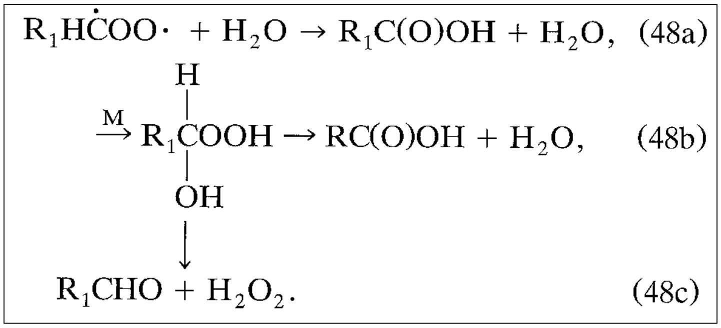
- Contain excess energy (from broken bonds)
  - Stabilized by collision
  - Decompose in various ways
    - Some to radicals and some to stable products
  - Example of Criegee from 1-propene + O_3

$$\begin{aligned}
(\mathrm{H\dot{C}HOO\cdot})^* + \mathrm{M} &\xrightarrow{0.37} \mathrm{H\dot{C}HOO\cdot} + \mathrm{M}, && (45a)\\
&\xrightarrow{0.12} \mathrm{HCO} + \mathrm{OH}, && (45b)\\
&\xrightarrow{0.38} \mathrm{CO} + \mathrm{H_2O}, && (45c)\\
&\xrightarrow{0.13} \mathrm{CO_2} + \mathrm{H_2}, && (45d)\\
&\xrightarrow{0} \mathrm{CO_2} + 2\mathrm{H}, && (45e)\\
&\xrightarrow{0} \mathrm{HCOOH}. && (45f)
\end{aligned}$$

"Stabilized Criegee Intermediate"

Fate of Stabilized Criegee Intermediates

- React with H_2O, SO_2, NO, NO_2, CO, aldehydes, and ketones
  - All reactions lead to stable products
  - Reaction with H_2O dominates



$$\begin{array}{ll} R_1H\dot{C}OO\cdot + H_2O \rightarrow R_1C(O)OH + H_2O, & (48a) \\ \qquad \xrightarrow{M} R_1\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}OOH \rightarrow RC(O)OH + H_2O, & (48b) \\ \qquad\qquad \downarrow & \\ R_1CHO + H_2O_2. & (48c) \end{array}$$

  - Others more uncertain, SO_2 & NO may be important in urban atmospheres

Importance of OH generation

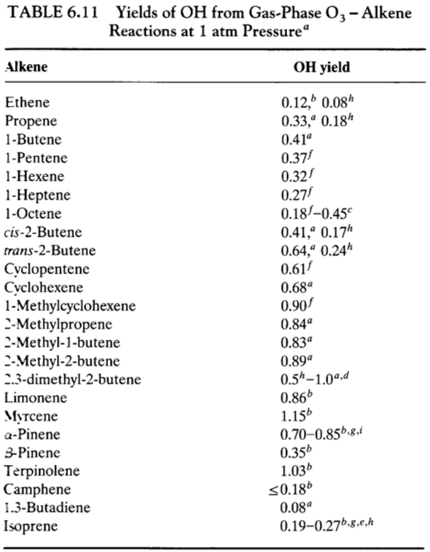


TABLE 6.11 Yields of OH from Gas-Phase O_3 – Alkene Reactions at 1 atm Pressure[a]

Alkene	OH yield
Ethene	0.12,[b] 0.08[h]
Propene	0.33,[a] 0.18[h]
1-Butene	0.41[a]
1-Pentene	0.37[f]
1-Hexene	0.32[f]
1-Heptene	0.27[f]
1-Octene	0.18[f]–0.45[c]
cis-2-Butene	0.41,[a] 0.17[h]
trans-2-Butene	0.64,[a] 0.24[h]
Cyclopentene	0.61[f]
Cyclohexene	0.68[a]
1-Methylcyclohexene	0.90[f]
2-Methylpropene	0.84[a]
2-Methyl-1-butene	0.83[a]
2-Methyl-2-butene	0.89[a]
2,3-dimethyl-2-butene	0.5[h]–1.0[a,d]
Limonene	0.86[b]
Myrcene	1.15[b]
α-Pinene	0.70–0.85[b,g,i]
β-Pinene	0.35[b]
Terpinolene	1.03[b]
Camphene	≤0.18[b]
1,3-Butadiene	0.08[a]
Isoprene	0.19–0.27[b,g,e,h]

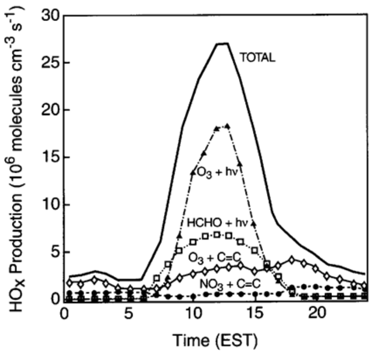


FIGURE 6.6 Calculated rates of HO_x radical generation from various sources for a rural forested site in the southeastern United States (adapted from Paulson and Orlando, 1996).

Especially important at night because no photolytic OH sources

Tropospheric Oxidation & + Ozone Formation III

<u>Required</u> Reading: Jacob Chapters 11 & 12

Atmospheric Chemistry
ATOC-5151 / CHEM 5151
Prof. Jose-Luis Jimenez
Spring 2013
Lecture by Doug Day

NO_3 + Alkenes

- NO_3 adds to double bond
- Excited adduct can:
  - Form epoxide
  - Stabilize, form peroxy radical, blah blah…

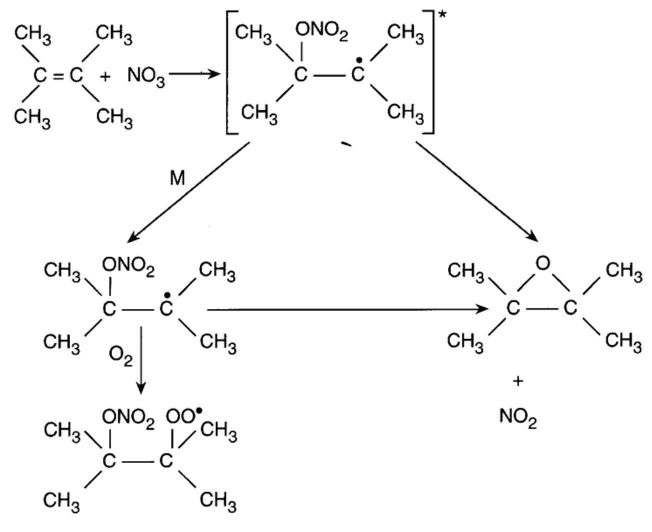


FIGURE 6.8 Mechanism of the NO_3 reaction with 2,3-dimethyl-2-butene (adapted from Skov *et al.*, 1994).

Schemes from F-P&P

NO_3 Reaction Rates

- Remember that collision rate ~2.5 x 10^{-10}
- Reactions are quite fast for biogenic alkenes
  - Comparable rates to OH
- d[Org]/dt = - k[Oxidant][Org]
  - NO_3: 50 ppt @ night
  - OH: 0.1 ppt @ day
- NO_3 reactions with biogenic alkenes @ night are very important

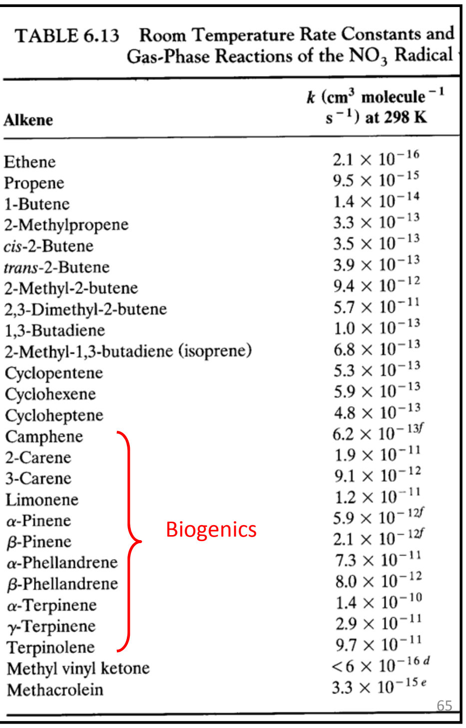


TABLE 6.13 Room Temperature Rate Constants and Gas-Phase Reactions of the NO_3 Radical

Alkene	k (cm^3 molecule^{-1} s^{-1}) at 298 K
Ethene	2.1×10^{-16}
Propene	9.5×10^{-15}
1-Butene	1.4×10^{-14}
2-Methylpropene	3.3×10^{-13}
cis-2-Butene	3.5×10^{-13}
trans-2-Butene	3.9×10^{-13}
2-Methyl-2-butene	9.4×10^{-12}
2,3-Dimethyl-2-butene	5.7×10^{-11}
1,3-Butadiene	1.0×10^{-13}
2-Methyl-1,3-butadiene (isoprene)	6.8×10^{-13}
Cyclopentene	5.3×10^{-13}
Cyclohexene	5.9×10^{-13}
Cycloheptene	4.8×10^{-13}
Camphene	6.2×10^{-13f}
2-Carene	1.9×10^{-11}
3-Carene	9.1×10^{-12}
Limonene	1.2×10^{-11}
α-Pinene	5.9×10^{-12f}
β-Pinene	2.1×10^{-12f}
α-Phellandrene	7.3×10^{-11}
β-Phellandrene	8.0×10^{-12}
α-Terpinene	1.4×10^{-10}
γ-Terpinene	2.9×10^{-11}
Terpinolene	9.7×10^{-11}
Methyl vinyl ketone	$<6 \times 10^{-16d}$
Methacrolein	3.3×10^{-15e}

Biogenics

Table from F-P&P

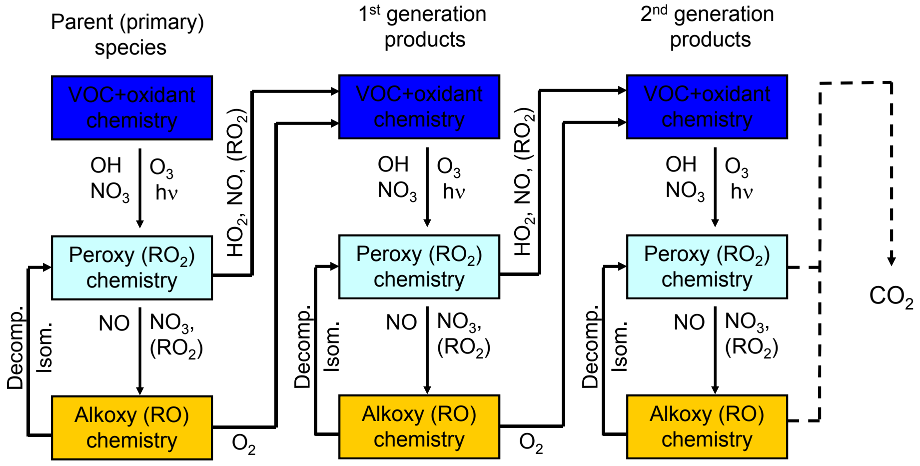
What about other organics?

- Similar types of radical chemistries
  - Aromatics: OH-addition
  - Aldehydes: aldehydic H-abstraction
  - Ketones and alcohols: alkyl chain H-abstraction
  - Carboxylic acids: OH-addition or H-abstraction
- Similar types of downstream chemistries
  - Gets really complicated quickly
- You should be able to understand it from what we have covered
  - If need to know for your research:
    - See the book for introduction
    - Then search the literature

General rules for atmospheric oxidation of VOCs

- Attack by OH is by H abstraction for saturated VOCs, by addition for unsaturated VOCs
- Reactivity increases with number of C-H bonds, number of unsaturated bonds
- Organic radicals other than peroxy react with O_2 (if they are small) or decompose (if they are large); O_2 addition produces peroxy radicals.
- Organic peroxy radicals (RO_2) react with NO and HO_2 (dominant), other RO_2 (minor); they also react with NO_2 but the products decompose rapidly (except in the case of peroxyacyl radicals which produce peroxyacylnitrates or PANs)
- RO_2+HO_2 produces organic hydroperoxides ROOH, RO_2+NO produces carbonyls (aldehydes RCHO and ketones RC(O)R') and also organic nitrates by a minor branch
- Carbonyls and hydroperoxides can photolyze (radical source) as well as react with OH
- Unsaturated HCs can also react with ozone, producing carbonyls and carboxylic acids
- RO_2+$R'O_2$ reactions produce a range of oxygenated organic compounds including carbonyls, carboxylic acids, alcohols, esters…

Big Picture of Organic Oxidation



Parent (primary) species

1st generation products

2nd generation products

VOC+oxidant chemistry

OH NO$_3$ | O$_3$ hν

Peroxy (RO_2) chemistry

NO | NO_3, (RO_2)

Alkoxy (RO) chemistry

Decomp.

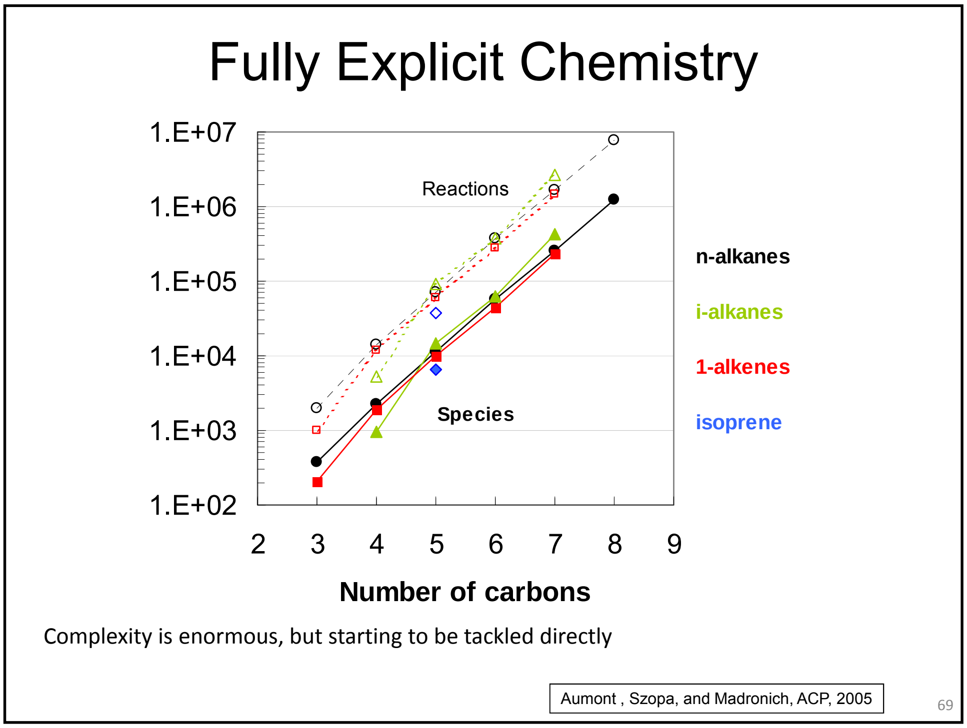
Isom.

HO_2, NO, (RO_2)

O_2

CO_2

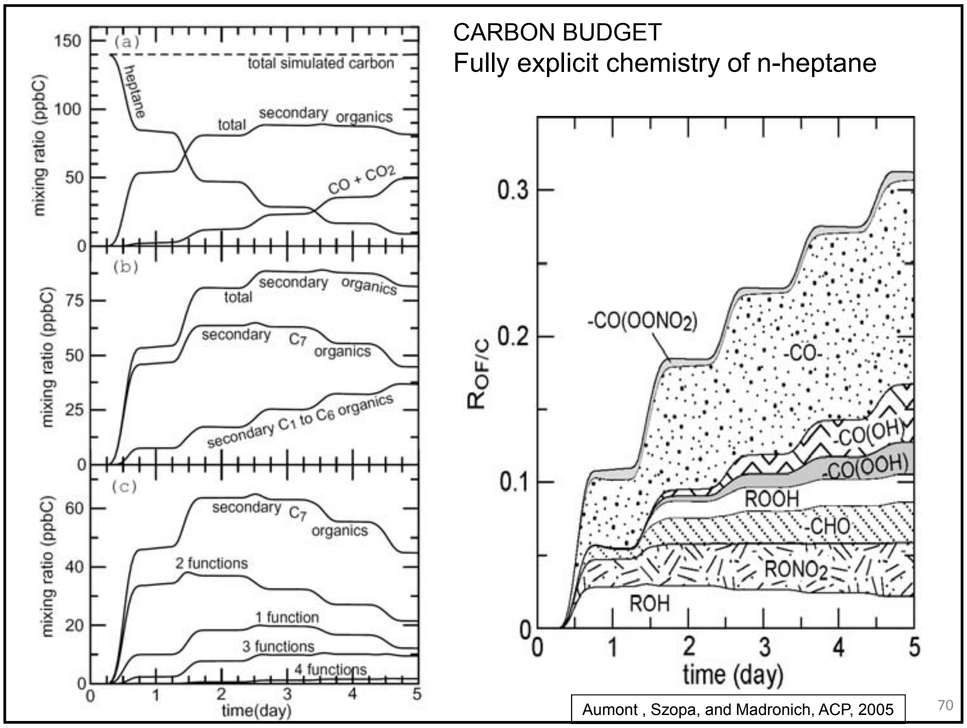
Aumont , Szopa, and Madronich, ACP, 2005



Fully Explicit Chemistry

Complexity is enormous, but starting to be tackled directly

Aumont , Szopa, and Madronich, ACP, 2005

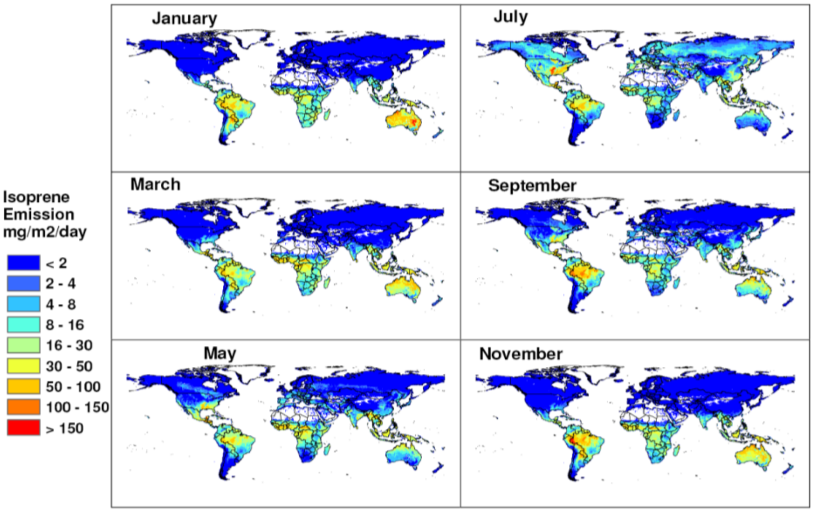


CARBON BUDGET
Fully explicit chemistry of n-heptane

Aumont , Szopa, and Madronich, ACP, 2005

Global Distribution of Isoprene Emissions

E = *f* (T, hν)

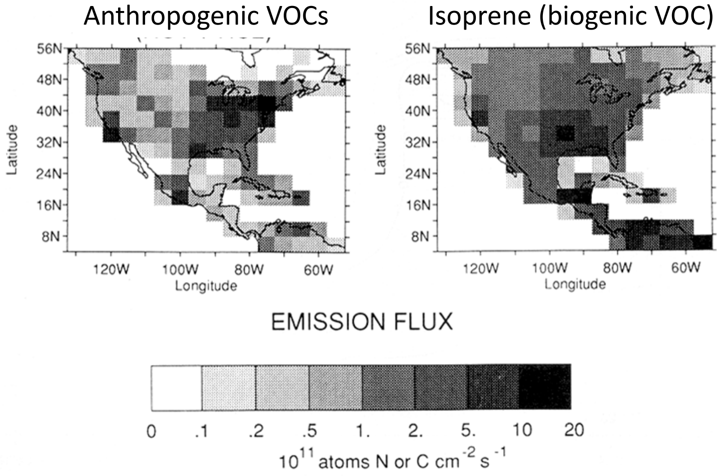


MEGAN biogenic emission model (Guenther et al., 2006)

From Jacob

Large Supply of Biogenic VOCs – unrecognized until the 1990s

Switches polluted areas in U.S. from NO_x-saturated to NO_x-limited regime! recognized in Revised Clean Air Act of 1999



Jacob et al., J. Geophys. Res. [1993]

From Jacob

Coupling of HO_x and NO_x Catalytic Cycles

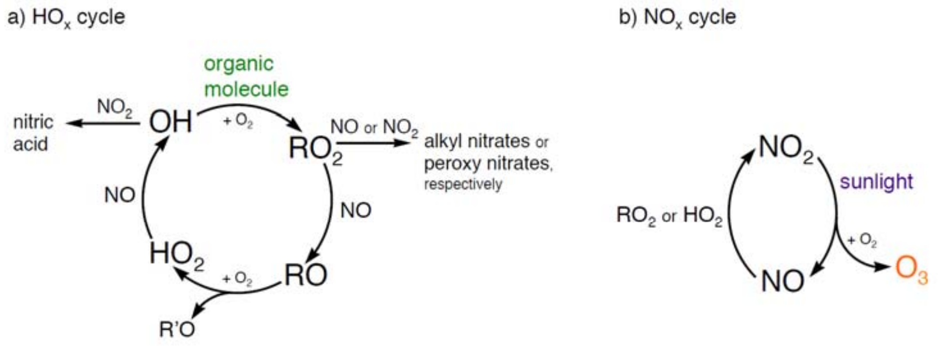
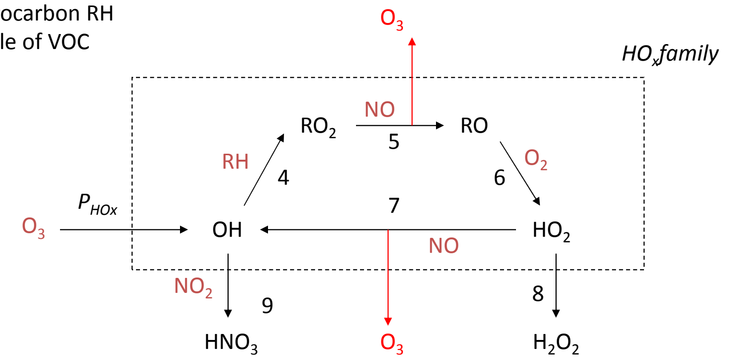


Fig. 1. Schematic of photochemical production of two new O_3 molecules from the oxidation of one generic organic molecule at the overlap of the HO_X **(a)** and NO_X **(b)** catalytic cycles. Only the NO_X termination channels are shown. HO_X chain terminations are reactions among peroxy radicals and OH.

Pusede & Cohen, ACP, 2012

Dependence of Ozone Production on NO_x and Volatile Organic Compounds (VOCs)

Take hydrocarbon RH as example of VOC



$$P(O_3) = \frac{2k_4 P_{HOx}[RH]}{k_9[NO_2][M]}$$

"NO_x- saturated" or
"VOC-limited" regime

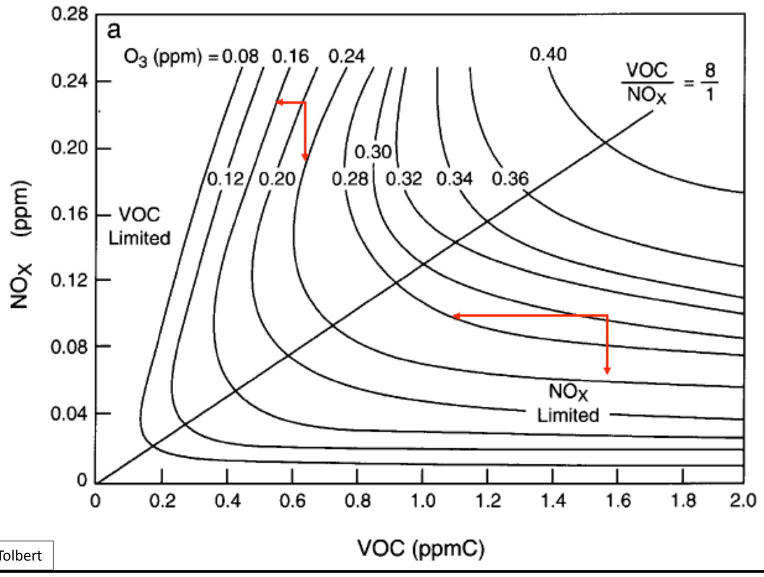
$$P(O_3) = 2k_7 \left(\frac{P_{HOx}}{2k_8}\right)^{1/2}[NO]$$

"NO_x-limited" regime

From Jacob

Ozone Concentrations vs. NO_x and VOC: Ozone “Isoplaths”

(for a typical urban airshed)



Adapted from Tolbert

Ozone Production Rate: NO_x Dependence for VOC Regimes

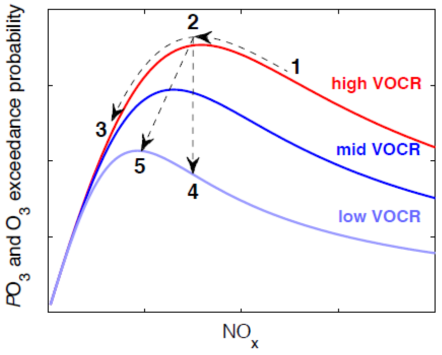
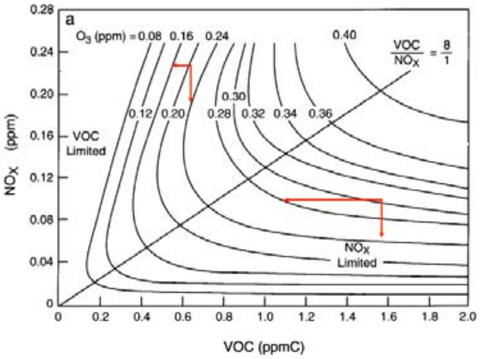


Fig. 2. The instantaneous ozone production rate (PO_3) and, by analogy the ozone exceedance probability, as a function of NO_x is shown for three categories of organic reactivity (VOCR): high (red), mid (blue), and low (violet). The mid- and high-VOCR curves correspond to scaling the base VOCR by 2 and 3, respectively. If temperature serves as an adequate proxy for VOCR then the three curves will also describe high- (red), moderate- (blue), and low- (violet) temperature regimes.

Pusede & Cohen, ACP, 2012

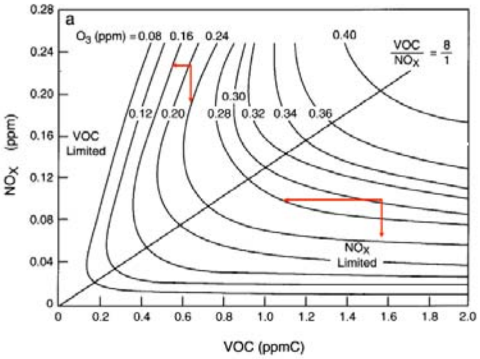
Ozone Regulatory Strategies



In rural areas it is most effective to regulate:
(assume some vegetation)

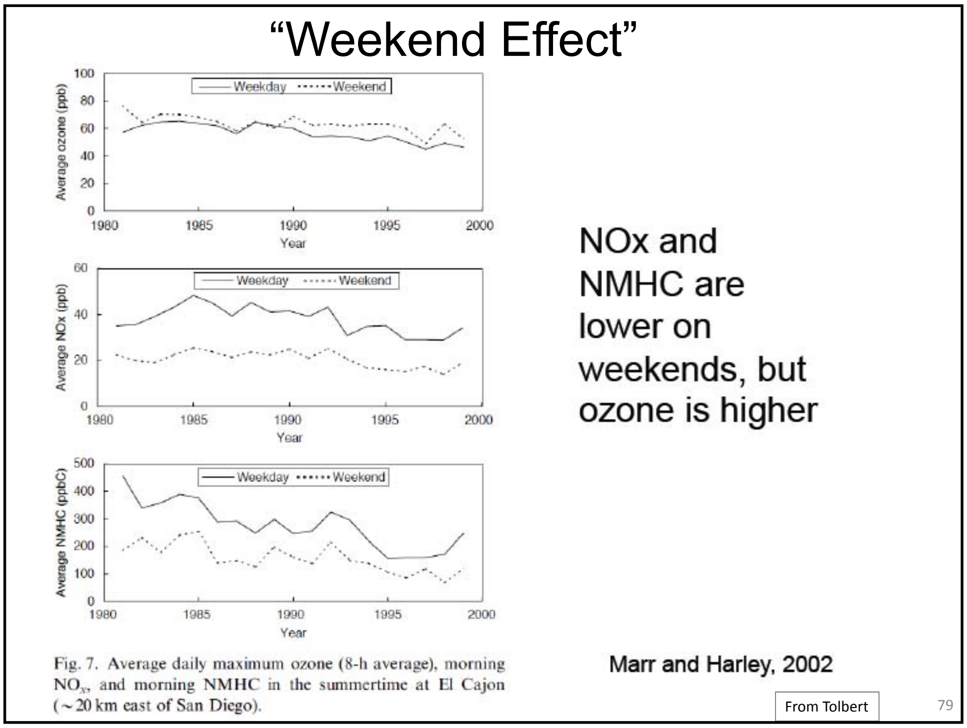
a) VOCs
b) NO_x
c) CO
d) Equally VOCs & NO_x
e) I don't know

Diesel vs Gasoline



In a very polluted urban area in the U.S. reducing diesel traffic may likely:
(hint: diesel engines make more NOx than gasoline engines)

a) Reduce ozone
b) Increase ozone
c) Increase NO_x
d) Decrease OH
e) I don't know



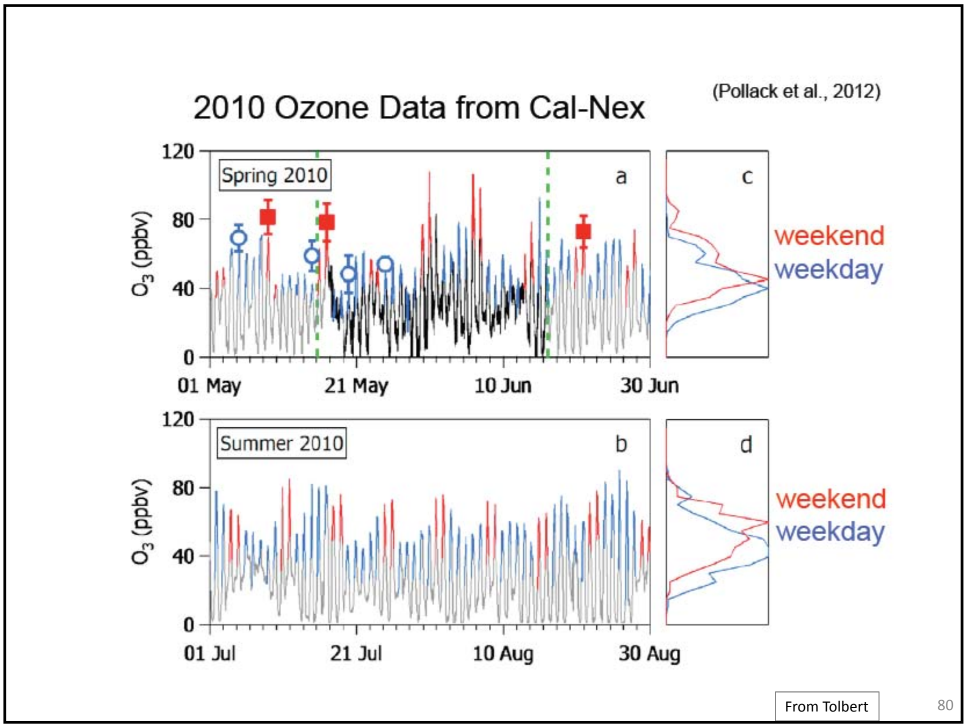
“Weekend Effect”

NOx and NMHC are lower on weekends, but ozone is higher

Fig. 7. Average daily maximum ozone (8-h average), morning NO_x, and morning NMHC in the summertime at El Cajon (~20 km east of San Diego).

Marr and Harley, 2002

From Tolbert

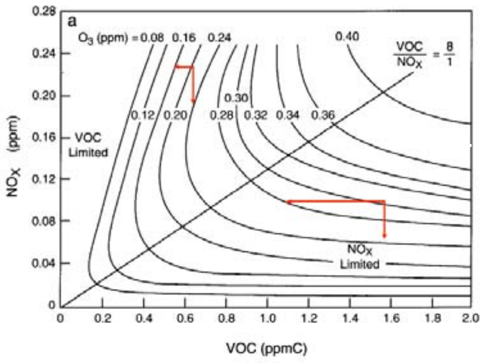


2010 Ozone Data from Cal-Nex

(Pollack et al., 2012)

From Tolbert

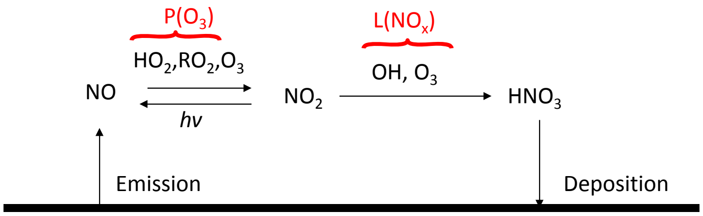
Evaporative Emissions



Reducing evaporative loss of gasoline at pumping stations in a polluted desert city (like Phoenix) should:

a) Reduce ozone
b) Increase ozone
c) Reduce NO$_x$
d) Have zero effect
e) I don't know

Even in NO$_x$-limited Regime, the Total O$_3$ Produced is VOC-dependent and [O$_3$] = f(E_{NOx}) is Strongly Nonlinear



Define ozone production efficiency (OPE) as the total number of O$_3$ molecules produced per unit NO$_x$ emitted.

Assuming NO$_x$ steady state, efficient HO$_x$ cycling, and loss of NO$_2$ by reaction with OH:

$$\mathbf{OPE} = \frac{P(O_3)}{L(NO_x)} = \frac{2k_7[HO_2][NO]}{k_9[NO_2][OH]} = \frac{2k_4[RH]}{k_9[NO_2]}$$

OPE ↘ as NO$_x$ ↗ ⇨ strong nonlinearity; in models, decreasing NO$_x$ emissions by 50% reduces ozone only by ~15%

From Jacob

Ozone vs. (NO_y - NO_x)

NO_x = NO+NO_2; NO_y = all oxidized nitrogen species; NO_z = NO_y-NO_x

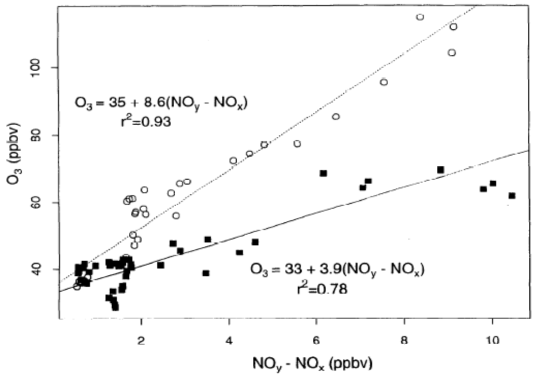


Figure 1. Scatterplots and linear regressions (reduced-major-axis method) of O_3 versus NO_y-NO_x concentrations at Harvard Forest, Massachusetts, for the weeks of May 6-12, 1990 (squares, solid line) and August 24-30, 1992 (circles, dotted line). Concentrations are hourly means at 1100-1700 EST.

Approximately how many HO_x cycles occurred for each NO_x molecule oxidized to NO_z in the August Observations:

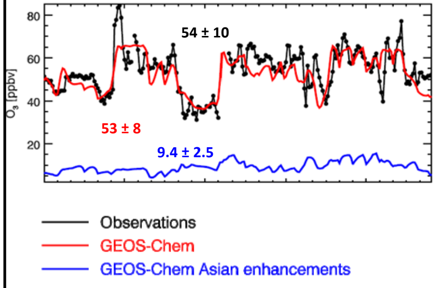
a) 3.9
b) 4.3
c) 8.6
d) 2.0
e) I don't know

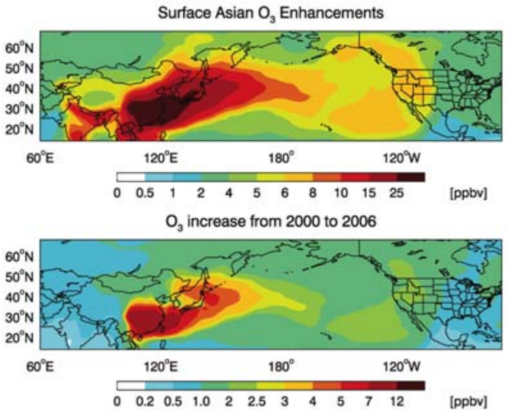
Hirsch et al. [1996]

Impact of Asian Emissions on Surface Ozone

Data from Dan Jaffe (University of Washington)

O_3 measurements at Mt. Bachelor
(44°N, 122°W, 2.7 km, in central Oregon)

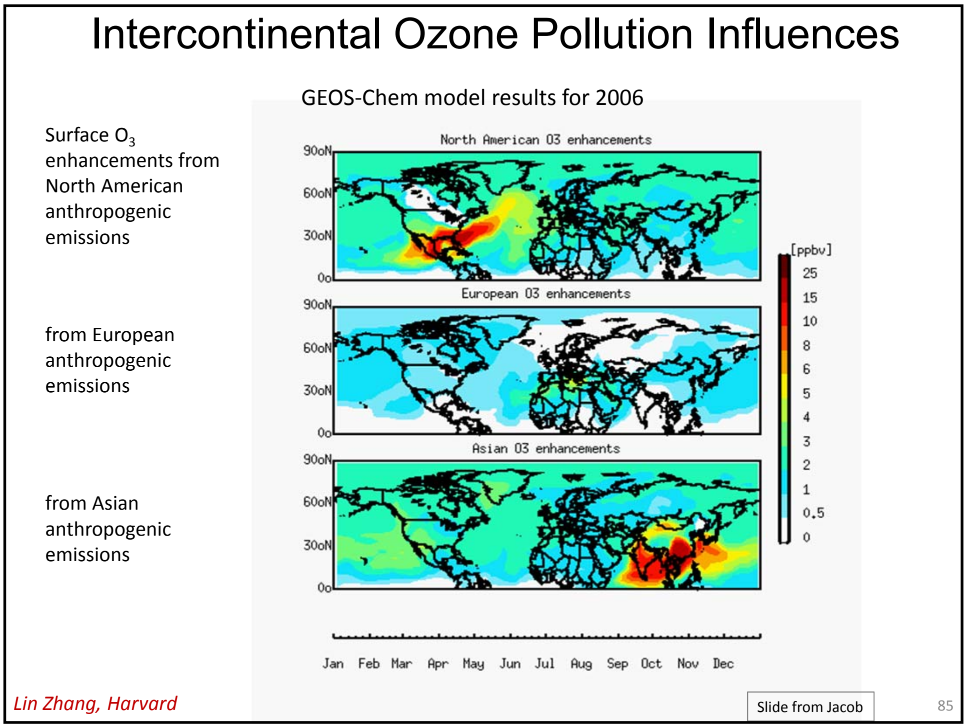




- Asian emissions increase surface ozone in the western US by 5-7 ppbv, compared with observed concentrations of ~50 ppbv.
- Doubling Asian emissions from 2000 to 2006 increases surface ozone by ~10 ppbv over Asia, and by 1-2 ppbv in the west US.

Zhang et al., 2008

Slide from Jacob



Intercontinental Ozone Pollution Influences

GEOS-Chem model results for 2006

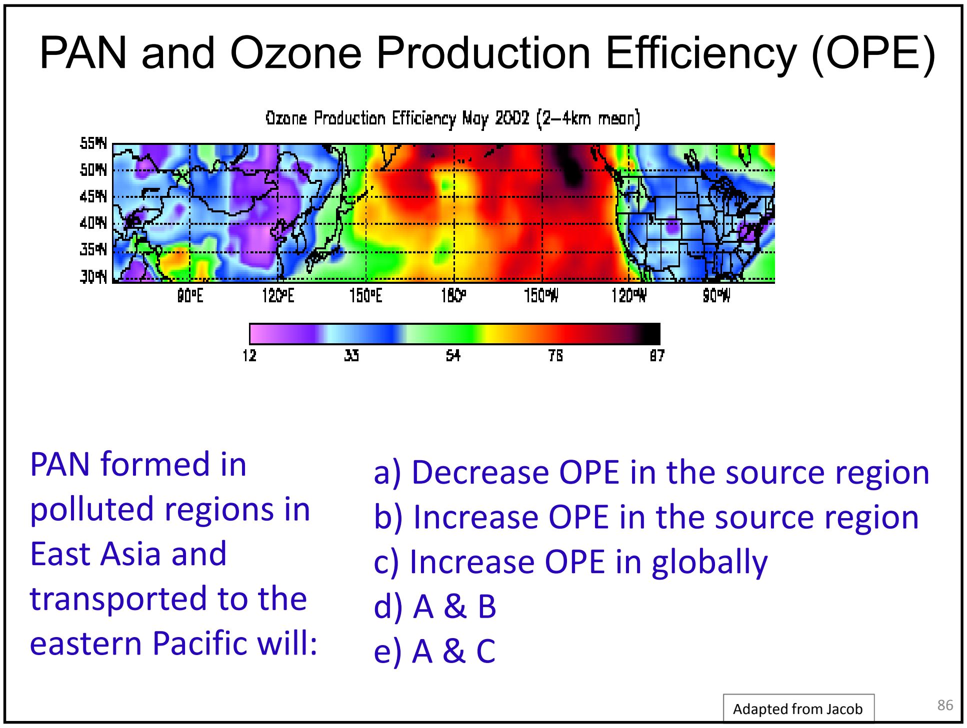
Surface O_3 enhancements from North American anthropogenic emissions

from European anthropogenic emissions

from Asian anthropogenic emissions

Lin Zhang, Harvard

Slide from Jacob

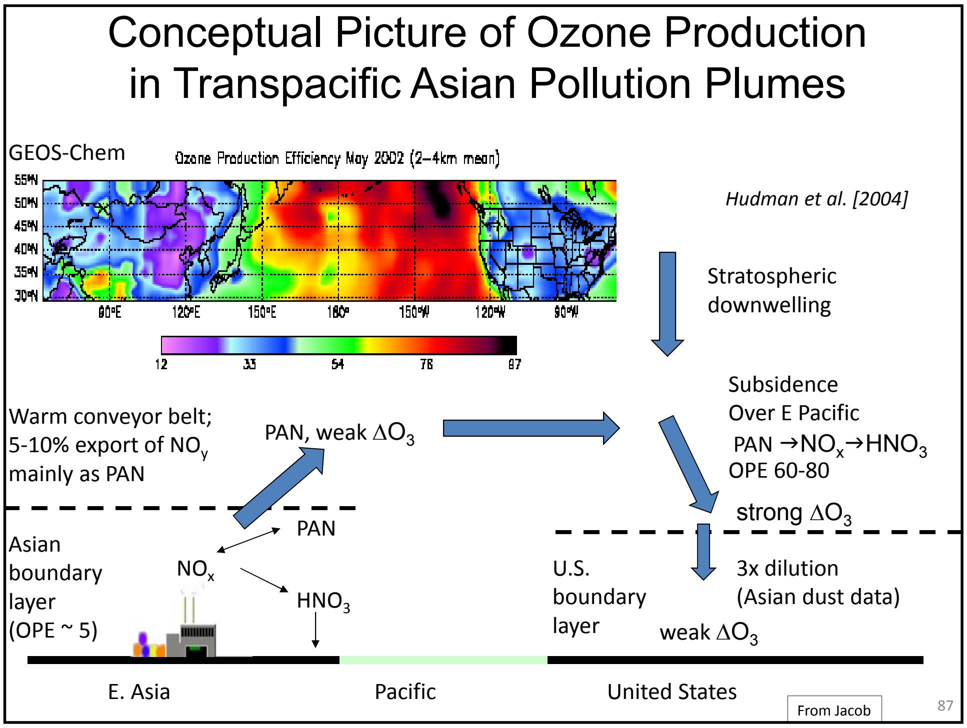


PAN and Ozone Production Efficiency (OPE)

PAN formed in polluted regions in East Asia and transported to the eastern Pacific will:

a) Decrease OPE in the source region
b) Increase OPE in the source region
c) Increase OPE in globally
d) A & B
e) A & C

Adapted from Jacob



Conceptual Picture of Ozone Production in Transpacific Asian Pollution Plumes

GEOS-Chem

Ozone Production Efficiency May 2002 (2–4km mean)

Hudman et al. [2004]

Stratospheric downwelling

Warm conveyor belt; 5-10% export of NO_y mainly as PAN

PAN, weak ΔO_3

Subsidence Over E Pacific
PAN → NO_x → HNO_3
OPE 60-80

strong ΔO_3

Asian boundary layer (OPE ~ 5)

PAN

NO_x

HNO_3

U.S. boundary layer

3x dilution (Asian dust data)

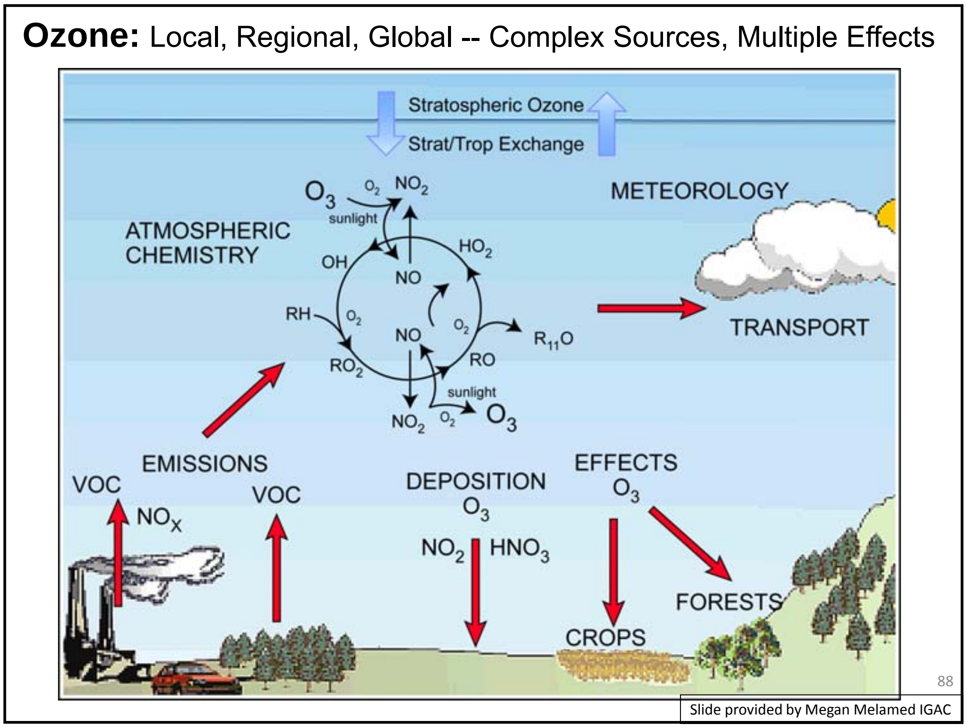
weak ΔO_3

E. Asia

Pacific

United States

From Jacob



Ozone: Local, Regional, Global -- Complex Sources, Multiple Effects

Slide provided by Megan Melamed IGAC