

Lecture 12: Gas Phase Organic- NO_x + UV Reactions

Required Reading: FP&P Chapter 6

Additional Reading: S&P Chapter 5

Catching-Up Reading: Jacob Chapters 11 & 12 (free online)

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2005
Prof. Jose-Luis Jimenez

Outline of Lecture

The big picture of atmospheric oxidation

A. Oxidants

B. Lifetimes of Organics

C. Reactions of Alkanes

D. “ “ of R, RO, and RO₂ Radicals

E. “ “ of Alkenes & Biogenics

F. “ “ of Aromatics

G. “ “ of O-Containing Organics

H. “ “ of N-Containing Organics

I. Chemistry of Remote Regions

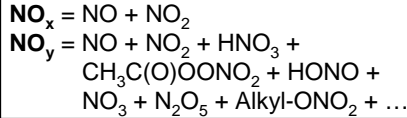
J. Atm. Chem. & Biomass Burning

• *We won't cover everything in class, read the rest in the book*

– *Have to know how to find + interpret quickly*

} Today

Emissions of NO_x



- ✓ Sources of NO_x are mainly anthropogenic (e.g., diesel engines)
- ✓ Most of NO_x is emitted as NO
- ✓ Lightning is an important natural source

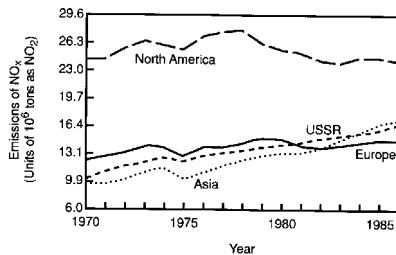


FIGURE 2.3 NO_x emissions in million tons of equivalent NO₂ for the period 1970 to 1986 for Asia, Europe, North America, and the USSR (from Hameed and Dignon, 1992).

TABLE 2.6 Typical Boundary Layer NO_x Mixing Ratios

Region	NO _x (ppb)
Urban-suburban	10–1000
Rural	0.2–10
Remote tropical forest	0.02–0.08
Remote marine	0.02–0.04

Source: National Research Council (1991).

TABLE 2.5 Estimated Global Emissions of NO, Typical of the Last Decade

Sources	Magnitude (Tg(N) yr ⁻¹)	Comments
Fossil-fuel combustion	24	Surface source; >95% NH
Soil release (natural and anthropogenic)	12	Continental surface source
Biomass burning	8	Tropical surface source
Lightning	5	Free tropospheric source
NH ₃ oxidation	3	Tropospheric source
Aircraft	0.5	6–12 km source; 95% NH
Transport from stratosphere	0.1 (0.6 total NO _x)	Free tropospheric source

Source: IPCC (1995).

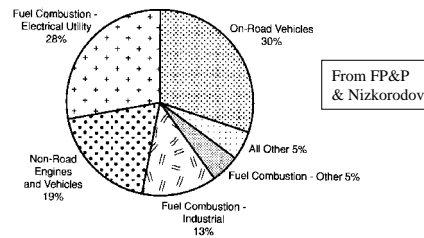


FIGURE 2.2 Contribution of various sources to total anthropogenic NO_x emissions in the United States in 1996 (from EPA, 1999).

VOC include

- Hydrocarbons
- Partially oxidized hydrocarbons

VOC do not include

- Methane
- Chlorofluorocarbons
- CO and CO₂

TABLE 2.11 Median Mixing Ratio of the 25 Most Abundant Nonmethane Organic Compounds Measured in the Summer 1987 Southern California Air Quality Study

Compound	Median Mixing Ratio in Parts per Billion of Carbon*
Ethane	27.1
Ethene	22.3
Acetylene	17.3
Propane	56.0
Propene	7.8
i-Butane	19.4
Butane	42.0
i-Pentane	52.4
Pentane	24.0
2-Methylpentane	16.0
3-Methylpentane	11.8
Hexane	10.8
Methylcyclopentane	10.1
Benzene	17.0
3-Methylhexane	7.4
Heptane	6.0
Methylcyclohexane	7.0
Toluene	49.1
Ethylbenzene	7.6
m- and p-Xylenes	25.2
o-Xylene	10.0
1,2,4-Trimethylbenzene	8.2
Formaldehyde	9.1
Acetaldehyde	14.8
Acetone	22.4

*Parts per billion of carbon (ppbC) is the parts per billion of carbon atoms in the molecule. It is simply the volume mixing ratio of the compound multiplied by the number of carbon atoms in the molecule.

Source: Lurmann and Main (1992).

From FP&P & Nizkorodov

Emissions of VOCs

- ✓ On global scale, biogenic emissions of VOC dominate
- ✓ Anthropogenic emissions account for 10-20% of the total but they are very important in urban areas, where they dominate.
- ✓ Atmosphere contains over 600 documented VOC

TABLE 2.10 Estimated Global Anthropogenic Emissions of Nonmethane Volatile Organic Compounds

Activity	Emission (Tg yr ⁻¹)
FUEL PRODUCTION/DISTRIBUTION	
Petroleum	8
Natural gas	2
Oil refining	5
Gasoline distribution	2.5
FUEL CONSUMPTION	
Coal	3.5
Wood	25
Crop residues (including waste)	14.5
Charcoal	2.5
Dung cakes	3
Road transport	36
Chemical industry	2
Solvent use	20
Uncontrolled waste burning	8
OTHER	
	10
Total	142

Source: Middleton (1995).

Atmospheric “Regimes”

	Urban Troposphere	Remote Troposphere	Stratosphere
NO_x levels	High	Low	Low
Organics	Petrochemical	Biogenic	None
UV flux	Low	Low	High
P	1 atm	1 atm to low	Very Low
T	“warm”	“warm” to low	low to “warm”

- Very different conditions in the different regions (“regimes”)
- Different set of reactions are important
- Why chemistry of these regions is often considered separately

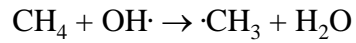
The Big Picture I

- **Organics + NO_x + UV → O₃, oxidants, particles**
- The details are complex
 - Next three lectures ~ 2 on organics, one on NO_x
- Organics
 - E.g. hydrocarbons like gasoline vapor (octane C₈H₁₈)
 - Burn rapidly at high temperature (2000 K) in an oxidizing atmosphere

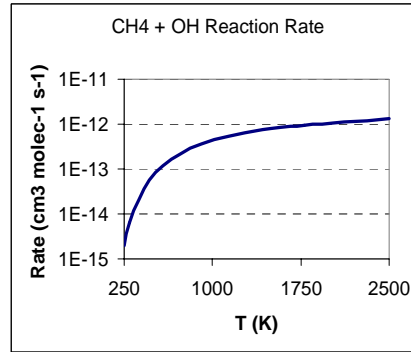
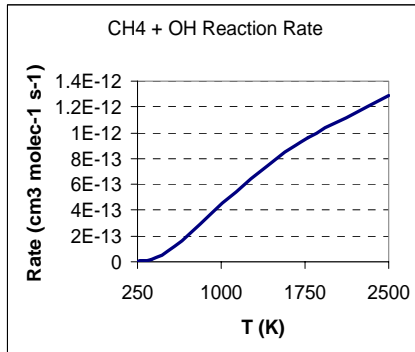
$$\text{C}_8\text{H}_{18} + 12.5 \text{O}_2 \rightarrow 8 \text{CO}_2 + 9 \text{H}_2\text{O} + \text{pollutants}$$
 - “Burn” slowly at low temperature
 - **“The Earth’s atmosphere is a low temperature flame”**
 - Organics end up mostly as CO₂ + H₂O
 - Not perfectly clean “flame”, intermediates and side products are pollutants

The atmosphere as a low T flame

- Reaction rates of as $f(T)$ for



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

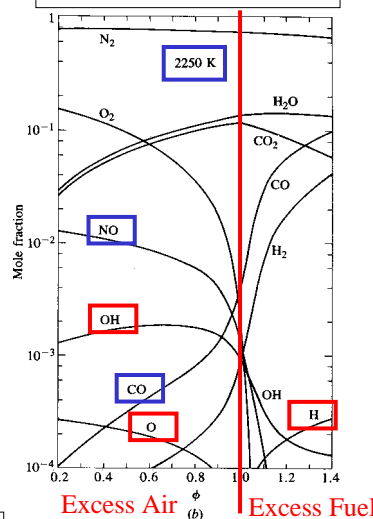


- What are the relative lifetimes of CH_4 at flame vs. ambient temperatures? Does this make sense?

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

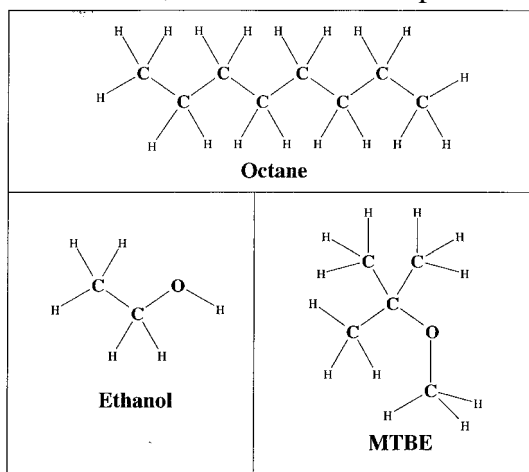


From Heywood, 1988, Internal Combustion Engine Fundamentals

$$\phi = \text{Fuel}/\text{Air} / (\text{Fuel}/\text{Air})_{\text{stoich}}$$

How do we proceed?

- $C_8H_{18} + 12.5 O_2 \rightarrow 8 CO_2 + 9 H_2O$ is an “overall reaction”
 - Many steps, but very fast in flame
 - In atmosphere, “very slow motion”, so intermediate steps + products are of great interest
 - We will follow the chemistry of various organic groups
 - A “nightmare” of details for all species

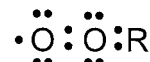
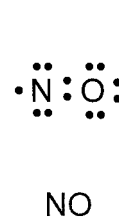
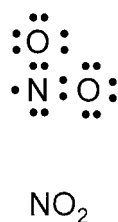
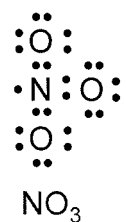
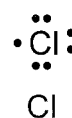
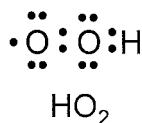
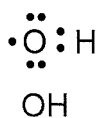


A

Radicals

- Radical = species with an unpaired electron

- High energy, high tendency to pair the electron to reduce the free energy
- Often rapid reactions

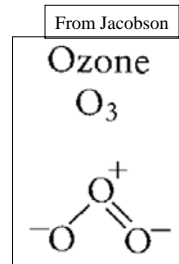


From Paul Ziemann

A

The Oxidants

- OH•
 - Fast rates, very low concentrations
 - H-abstraction: $\text{CH}_4 + \text{OH}\cdot \rightarrow \cdot\text{CH}_3 + \text{H}_2\text{O}$
 - Attacks most organics
 - Mostly during the day
- O₃
 - Slower rates, but high concentrations
 - Avid for electrons
 - Attacks double bonds C=C
 - Day & night
- NO₃•
 - Fast photolysis during day, important at night
 - “Count Dracula”
- HO₂• & Cl



A

Oxidant Sources in Troposphere I

Hydroxyl Radical (OH)

- Photodissociation of O₃

$$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D})$$

$$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH}\cdot$$
- Photodissociation of HONO and H₂O₂

$$\text{HONO} + h\nu \rightarrow \text{OH}\cdot + \text{NO}$$

$$\text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH}\cdot + \text{OH}\cdot$$
- Alkene oxidation

$$\text{R}_1\text{CH}=\text{CHR}_2 + \text{O}_3 \rightarrow \text{OH}\cdot + \text{prod.}$$
- From HO₂•
 - $\text{NO} + \text{HO}_2\cdot \rightarrow \text{NO}_2 + \text{OH}\cdot$

Hydroperoxyl Radical (HO₂)

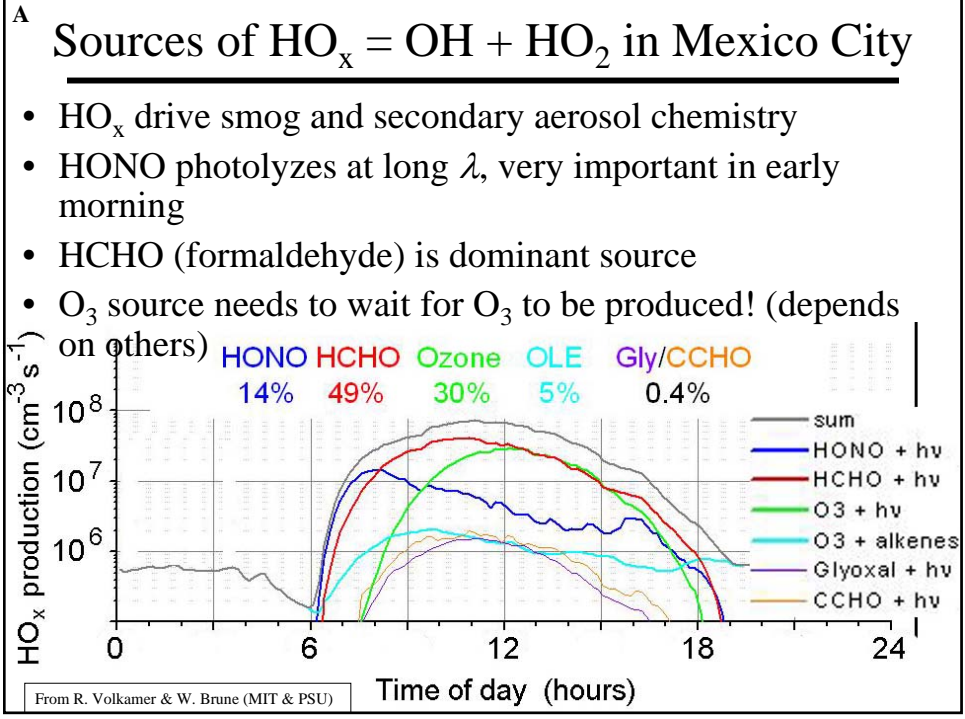
- Photodissociation of CH₂O

$$\text{CH}_2\text{O} + h\nu \rightarrow \text{H}\cdot + \text{HCO}\cdot$$

$$\text{H}\cdot + \text{O}_2 + \text{M} \rightarrow \text{HO}_2\cdot + \text{M}$$

$$\text{HCO}\cdot + \text{O}_2 \rightarrow \text{HO}_2\cdot + \text{CO}$$
- From alkoxy radical reactions

$$\text{RCH}_2\text{O}\cdot + \text{O}_2 \rightarrow \text{RCHO} + \text{HO}_2\cdot$$
 - Byproduct of oxidation of organics



A Oxidant Sources in Troposphere II

Ozone (O₃)

- Photodissociation of NO₂

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}\cdot$$

$$\text{O}\cdot + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$$

Nitrate Radical (NO₃·)

- Oxidation of NO₂

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3\cdot + \text{O}_2$$

Chlorine (Cl)

- Sea-salt chemistry

$$\text{N}_2\text{O}_5(\text{g}) + \text{NaCl}(\text{s}) \rightarrow \text{ClONO}_2(\text{g}) + \text{NaNO}_3(\text{s})$$

$$\text{ClONO}_2(\text{g}) + \text{NaCl}(\text{s}) \rightarrow \text{Cl}_2(\text{g}) + \text{NaNO}_3(\text{s})$$

$$\text{ClONO}_2 + h\nu \rightarrow \text{Cl}\cdot + \text{NO}_2$$

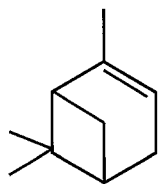
$$\text{Cl}_2 + h\nu \rightarrow \text{Cl}\cdot + \text{Cl}\cdot$$

Organic Compound Classes

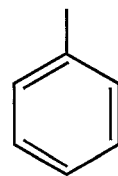
- Hydrocarbons: only C and H



Alkanes
(decane)



Alkenes/Monoterpenes
(α -pinene)



Aromatics
(toluene)

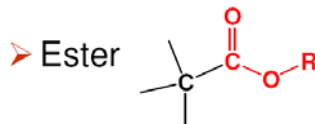
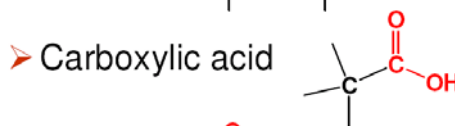
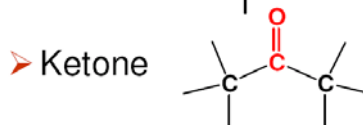
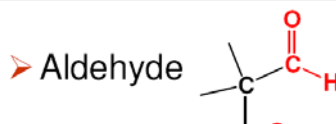
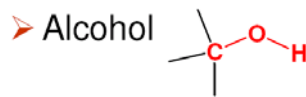
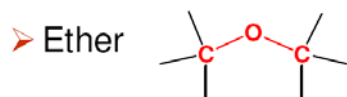
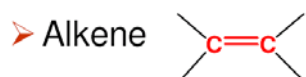
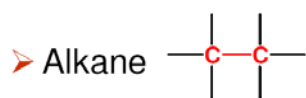
Mostly
Biogenic

Mostly
Anthropogenic

From Paul Ziemann

Organic Functional Groups

- FG: atom or group of atoms with specific structure and reactivity



<http://www.uwec.edu/carneymj/Adobe%20handouts/Nomenclature.pdf> (nice page for catching up on organic nomenclature)

B

Lifetimes of Organics

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



$$d[\text{Org}]/dt = -k[\text{X}][\text{Org}] ; \text{lifetime: } \tau = 1/k[\text{X}]$$

TABLE 6.1 Estimated Lifetimes of Representative Organics in the Troposphere^a

Organic	OH ($1 \times 10^6 \text{ cm}^{-3}$)	O ₃ (100 ppb)	NO ₃ (50 ppt)	HO ₂ ($2 \times 10^8 \text{ cm}^{-3}$, 8 ppt)	Cl ($1 \times 10^4 \text{ cm}^{-3}$)
<i>n</i> -Butane	5 days	≥ 1300 yr	205 days		5 days
<i>trans</i> -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 $\tau = 1/k_p[\text{oxidant}] = \text{time for the organic to fall to } 1/e \text{ of its initial value; except as shown here, rate constants are found in text.}$

^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 $k(\text{Cl} + \text{C}_2\text{H}_2) = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from $k_0 = 5.7 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, $k_{\infty} = 2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $F_{\text{Cl}} = 0.6$ (Atkinson *et al.*, 1997a).

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

From F-P&P

C

Alkanes + OH·

- OH· has strong tendency to abstract H
 - $\text{RH} + \text{OH}\cdot \rightarrow \text{R}\cdot + \text{H}_2\text{O}$
 - We will focus on R· soon
- Rate increases with size and complexity
 - Maximum rate?
- CH₄ is far slower than others
 - Focus on Non-Methane Hydrocarbons (NMHC) for urban smog
 - Why CH₄ survives and builds up to be a greenhouse gas

TABLE 6.2 Rate Constants and Temperature

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

C

Alkanes + Cl·

- Cl· also likes to abstract H

$$\text{RH} + \text{Cl}\cdot \rightarrow \text{R}\cdot + \text{HCl}$$
- Also forms an alkyl radical
- Reactions compared with collision rate?
- Importance vs. OH chemistry?

TABLE 6.4 Rate Constants of Cl Atoms with Alkanes

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

^a From Atkinson (1997a); temperature dependence given by $k = Ae^{-E_a/RT}$.

From F-P&P

D

Fates of alkyl radicals (R·)

- Radical nomenclature:
 - Alkyl: R·
 - Alkylperoxide: R-O-O· or RO₂·
 - 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 O₂

$$\text{R}\cdot + \text{O}_2 + \text{M} \rightarrow \text{RO}_2\cdot + \text{M}$$
- $k \sim 1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
 - Lifetime of R· at ground level?

D

Alkylperoxy Radicals (RO₂·) I

- React mainly with NO, HO₂·, RO₂·, and NO₃
- RO₂· + NO →
 - Fast: $k \sim 8 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
 - Do not vary much with R
 - Products
 - Mainly → RO· + NO₂
 - Again: this is how we make O₃ in the troposphere
 - Also → RONO₂ (alkyl nitrate)
 - Yields increase with RO₂· size
- CH₃O₂· + NO₃· → CH₃O· + NO₂ + O₂
 - Fast $k \sim 2 \times 10^{-12}$, important @ night

TABLE 6.5 Yields of RONO₂ in RO₂ + 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
<i>n</i> -Butane	
1-Butyl	≤0.04
2-Butyl	0.083
Isobutane	
2-Methyl-1-propyl	0.075
<i>tert</i> -Butyl	0.18
<i>n</i> -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
<i>n</i> -Pentane	
<i>n</i> -Pentyl	0.51

From F-P&P

D

Alkylperoxy Radicals (RO₂·) II

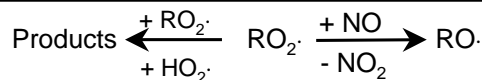
- RO₂· + HO₂· → ROOH + O₂ (24a)
- Carbonyl + H₂O + O₂ (24b)
- ROH + O₃ (24c)
 - ROOH is hydroperoxide R-O-O-H
 - Mostly by (24a) for small R, other channels contribute for larger R
 - $k \sim 6 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ @ room T
- RO₂· + RO₂· → 2RO· + O₂ (25a)
- ROH + RCHO + O₂ (25b)
- ROOR + O₂ (25c)

TABLE 6.6 Recommended Rate Constants and Branching Ratios at Room Temperature for the Self-Reactions of Some RO₂ Radicals^a

From F-P&P

RO ₂	$k_{12}^{298\text{K}}$ (cm ³ molec ⁻¹ s ⁻¹)	Branching ratios		
		(25a) (2RO + O ₂)	(25b) (ROH + RCHO + O ₂)	(25c) (ROOR + O ₂)
CH ₃ O ₂	3.7×10^{-13}	0.33 ± 0.05^b	$\sim 0.67^f$	Minor
HOCH ₂ CH ₂ O ₂	2.3×10^{-12}	0.30 ± 0.08^c	$\sim 0.70^f$	$< 0.006^d$
C ₂ H ₅ O ₂	6.4×10^{-14}	0.41 ± 0.04^d	0.50	0.05 ^e
		0.50^e	$0.63 + 0.06^{b,c}$	0.32^e

D Relative Importance of RO₂· Reactions



Critical parameter is the ratio of the corresponding reaction rates:

$$\begin{aligned} k(\text{CH}_3\text{O}_2 + \text{NO}) &\approx 7.7 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} @ 298 \text{ K} \\ k(\text{CH}_3\text{O}_2 + \text{HO}_2) &\approx 5.6 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} @ 298 \text{ K} \\ k(\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2) &\approx 4.7 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} @ 298 \text{ K} \end{aligned}$$

$$\begin{aligned} [\text{NO}]_{\text{urban}} &\approx 20 \text{ ppb} = 5 \times 10^{11} \text{ molec cm}^{-3} \\ [\text{HO}_2]_{\text{urban}} &\approx [\text{CH}_3\text{O}_2]_{\text{urban}} \approx 40 \text{ ppt} = 10^9 \text{ molec cm}^{-3} \\ \{\text{Rate}(\text{CH}_3\text{O}_2 + \text{NO}) / \text{Rates}(\text{RO}_2 + \text{CH}_3\text{O}_2)\}_{\text{urban}} &\approx 4000 \end{aligned}$$

$$\begin{aligned} [\text{NO}]_{\text{clean}} &\approx 1 \text{ ppt} \approx 2 \times 10^7 \text{ molec cm}^{-3} \\ [\text{HO}_2]_{\text{clean}} &\approx [\text{CH}_3\text{O}_2]_{\text{clean}} \approx 5 \text{ ppt} \approx 10^8 \text{ molec cm}^{-3} \\ \{\text{Rate}(\text{CH}_3\text{O}_2 + \text{NO}) / \text{Rates}(\text{RO}_2 + \text{CH}_3\text{O}_2)\}_{\text{clean}} &\approx 1 \end{aligned}$$

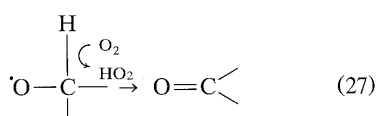
From S. Nizkorodov

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

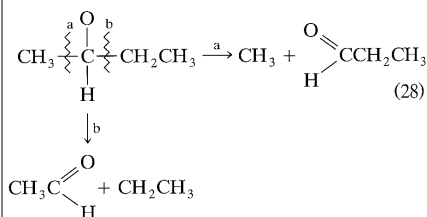
D Alkoxy Radicals (RO·)

From F-P&P

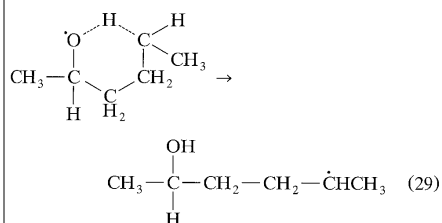
- Three main fates
- Reaction with O₂



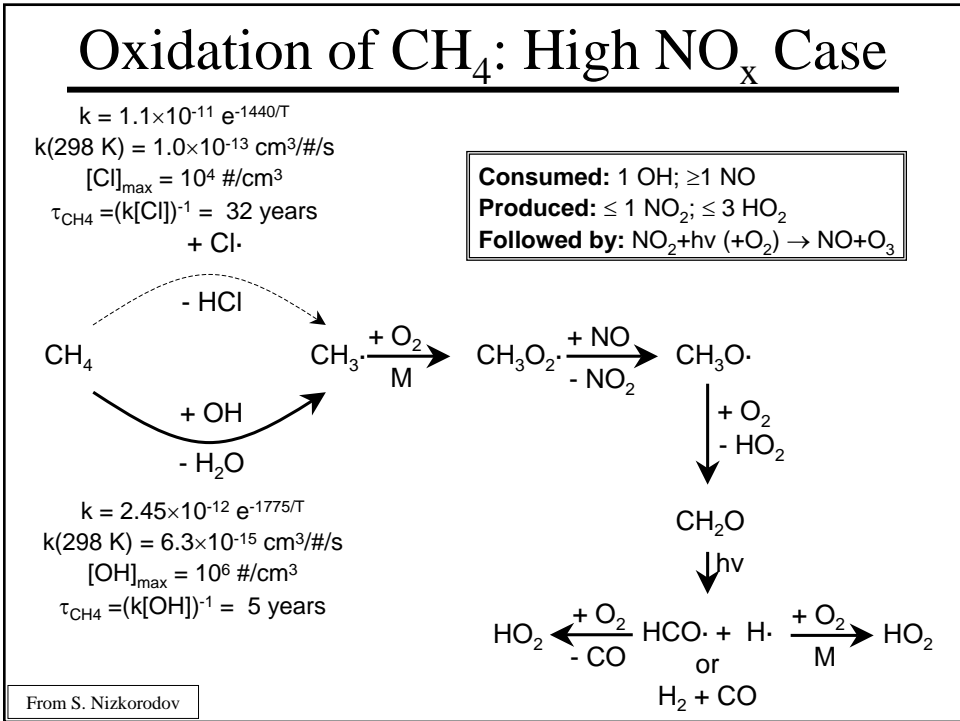
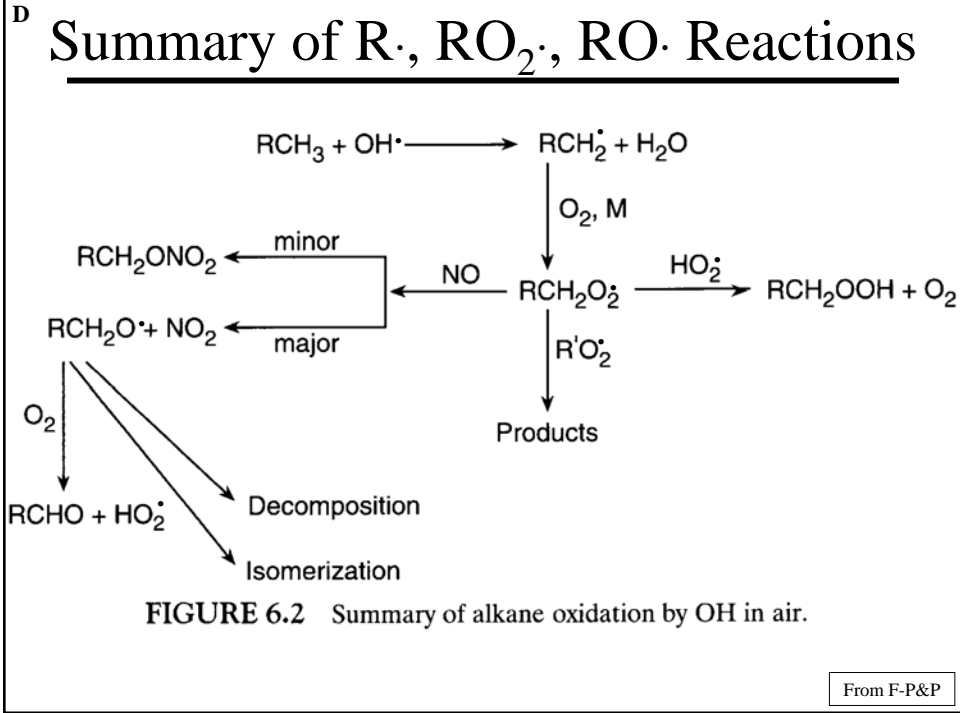
- Decomposition



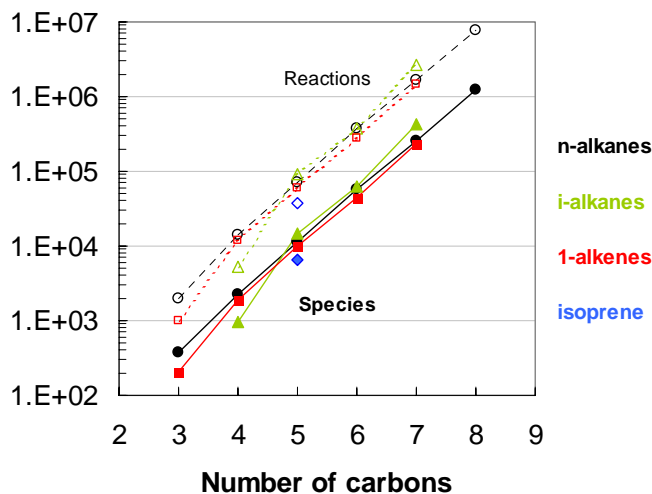
- Intramolecular isomerization



- Where isomerization is possible, it dominates
 - ↑ as R size increases
- Otherwise RO· + O₂

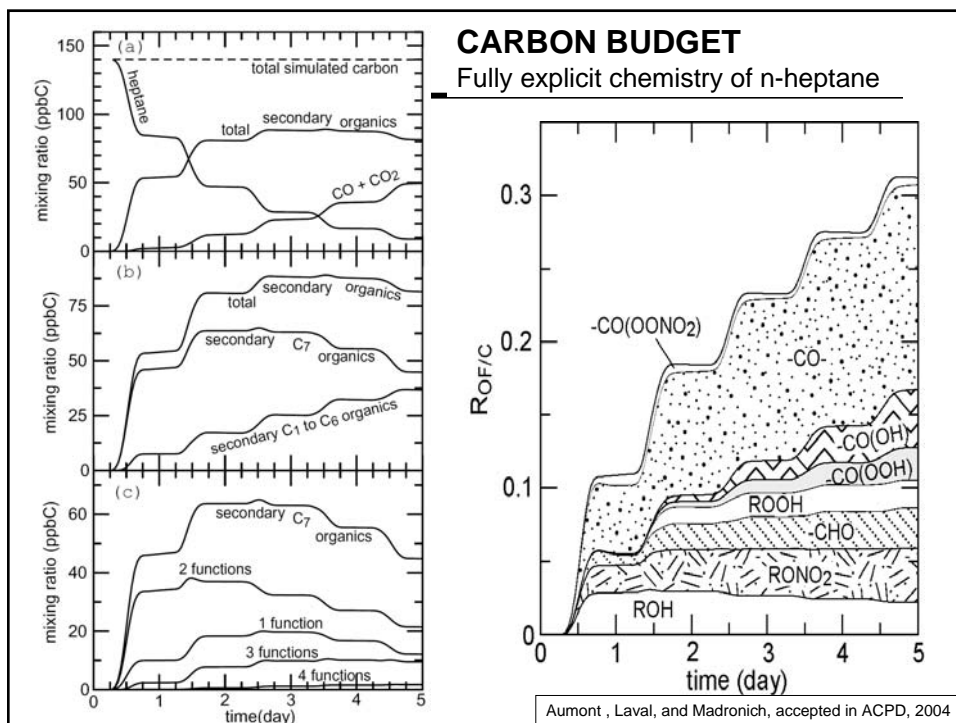


Fully Explicit Chemistry



Complexity is enormous, but starting to be tackled directly

Aumont, Laval, and Madronich, accepted in ACPD, 2004



Aumont, Laval, and Madronich, accepted in ACPD, 2004