

Lecture 13: Gas Phase Organic- NO_x + UV Reactions II

Required Reading: FP&P Chapter 6 (except as noted next)

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

All figures
from F-P&P

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 Alkynes~~

~~G. “ “ of Aromatics~~

~~H. “ “ of O-Containing Organics~~

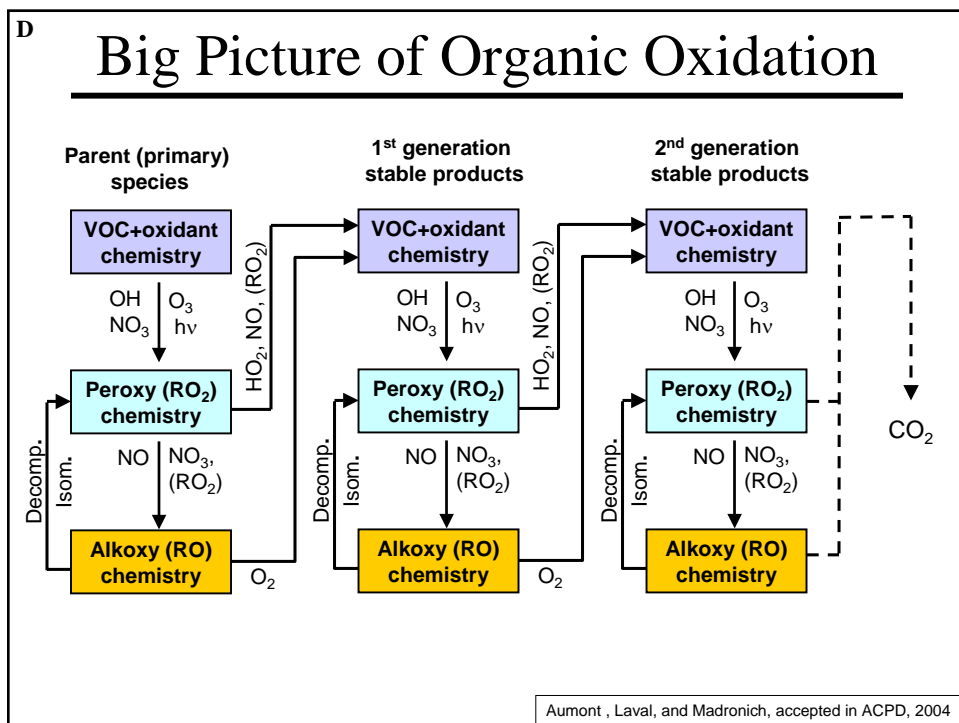
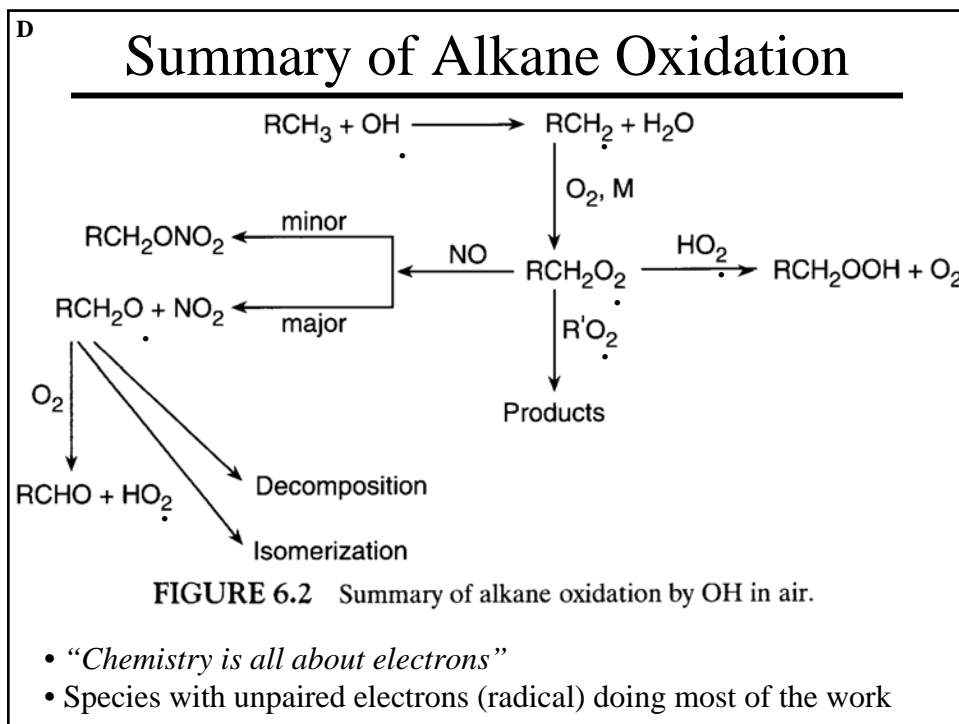
~~I. “ “ of N-Containing Organics~~

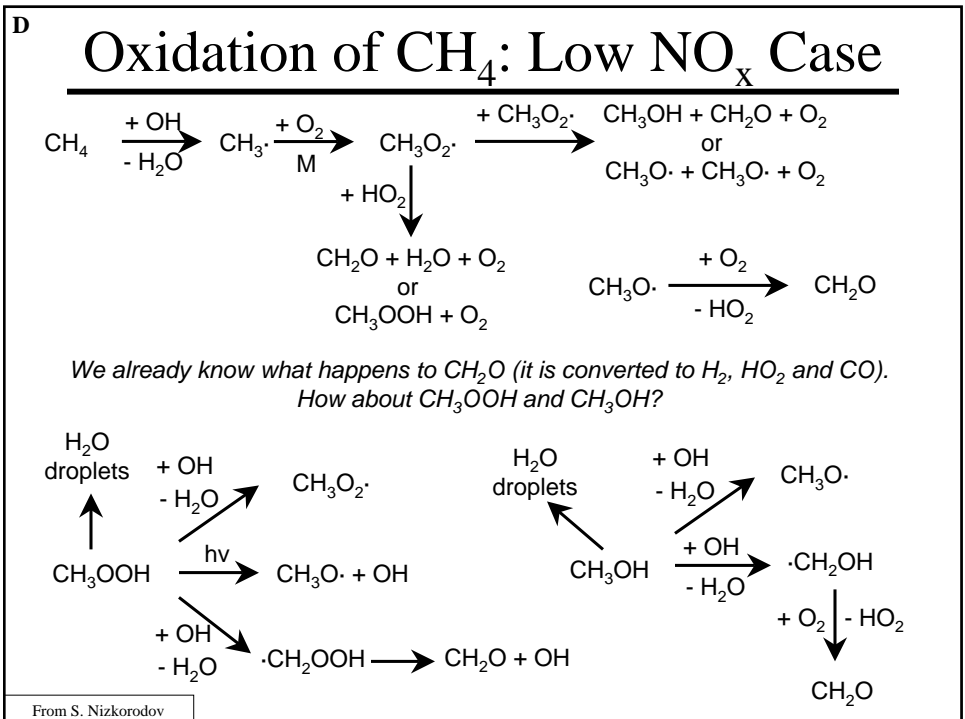
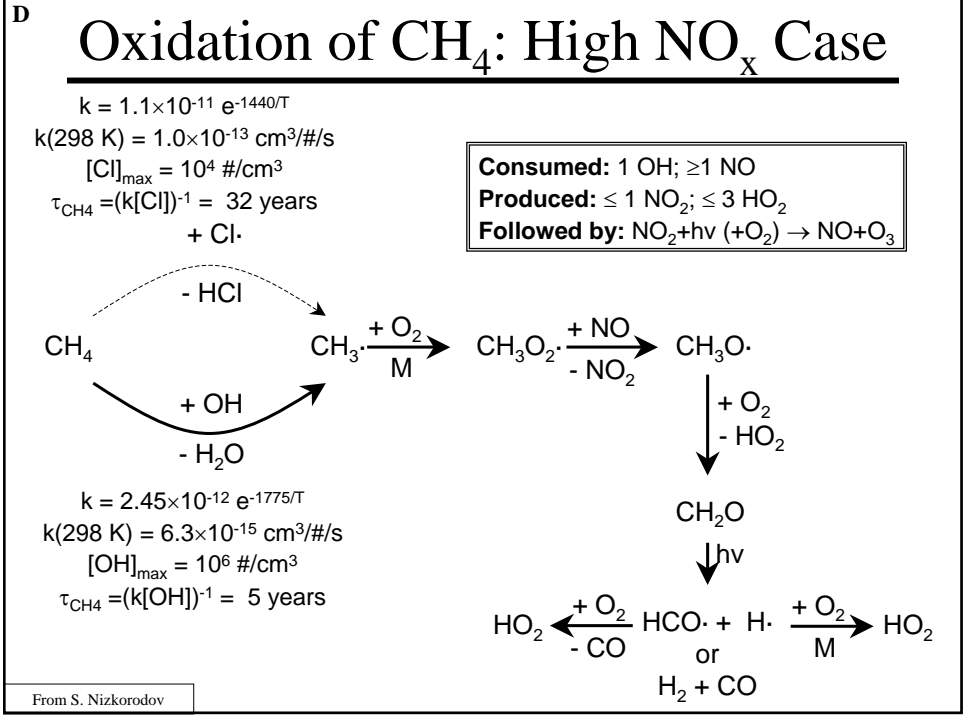
J. Chemistry of Remote Regions

K. Atm. Chem. & Biomass Burning

Last Lecture

Today





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).

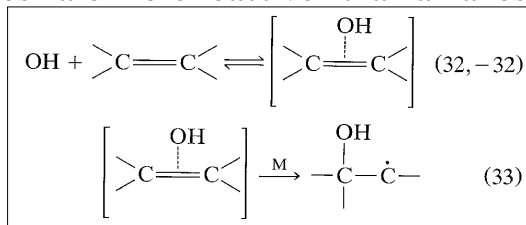
^d Using $k = 6.8 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1994).

From F-P&P

E

Reactions of Alkenes

- E.g. HC₃-CH=CH-CH₃, 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, O₃, NO₃, Cl
 - “The double bond gets the whole molecule in trouble”
 - Alkenes “are more reactive” than alkanes



E Alkenes + OH

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

| Alkene | k° (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 |
| <i>cis</i> -2-Butene | 56.4 | 11.0 | -487 |
| <i>trans</i> -2-Butene | 64.0 | 10.1 | -550 |
| 2-Methylpropene | 51.4 | 9.47 | -504 |
| 1-Pentene | 31.4 | | |
| <i>cis</i> -2-Pentene | 65 | | |
| <i>trans</i> -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 | | |
| <i>trans</i> -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 C₂H₄ and C₃H₆.

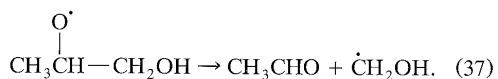
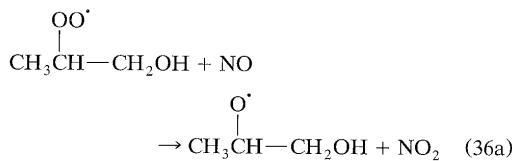
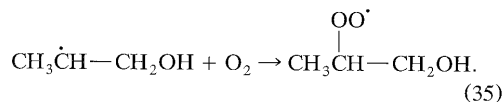
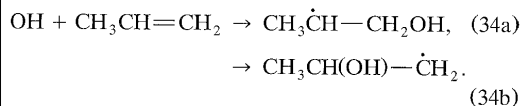
^d From Atkinson (1994).

^e See Fig. 6.22 for structures of biogenics.

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

E What happens after OH addition?

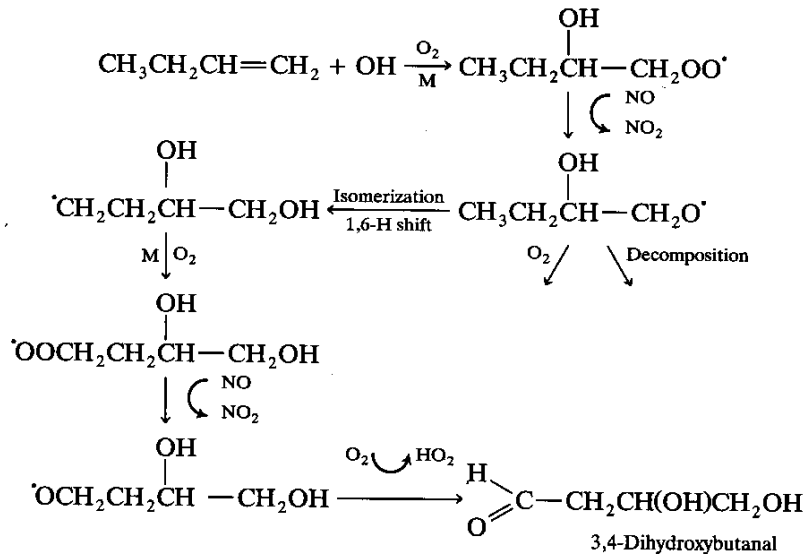
- Hydroxy group + alkyl radical
- Alkyl radical → Peroxy radical
- Peroxy radical → Alkoxy radical or (stable) nitrate
- Alkoxy radical → reaction with O₂, decomposition, isomerization



E

Example of β -hydroxyalkyl Isomerization

- As for alkanes, larger alkoxy radicals isomerize:



E

O_3 + Alkenes

- Remember that collision rate $\sim 2.5 \times 10^{-10}$
- Much slower reactions than for OH
- Compare
 - OH + Propene: 2.6×10^{-11}
 - O_3 + Propene: 1×10^{-17}
- But remember:
 - $-\text{d}[\text{Org}]/\text{dt} = -k[\text{Oxidant}][\text{Org}]$
 - 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 ($10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) | A ($10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) | 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 | | |

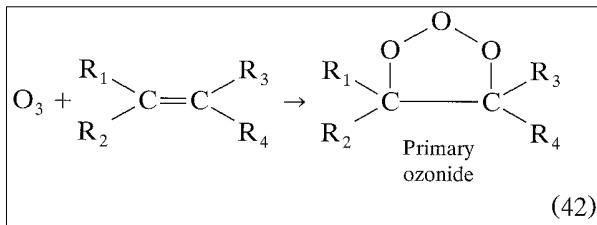
^a $k = Ae^{-E_a/RT}$.

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

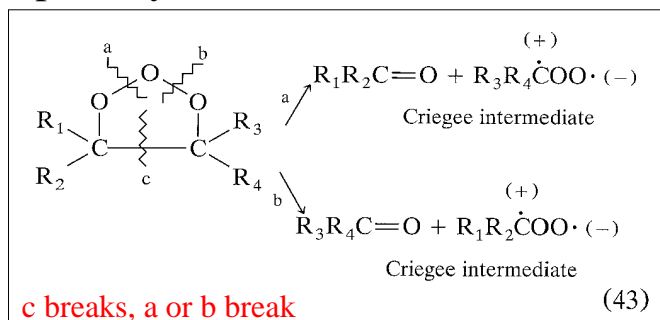
^c Average of Grosjean and Grosjean (1998a) and Neeb *et al.* (1998b).

E Mechanism of O₃ + Alkenes: First steps

- O₃ adds across the double bond

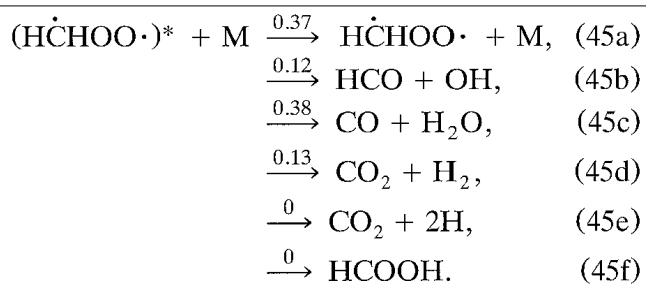


- The primary ozonide is not stable and breaks



E 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 + O₃



“Stabilized Criegee Intermediate”

E Fate of Stabilized Criegee Intermediates

- React with H₂O, SO₂, NO, NO₂, CO, aldehydes, and ketones
 - All reactions lead to stable products
 - Reaction with H₂O dominates



- Others more uncertain, SO₂ & NO may be important in urban atmospheres

E Importance of OH generation

- OH can react with all organics, not just alkenes!

TABLE 6.11 Yields of OH from Gas-Phase O₃ - Alkene Reactions at 1 atm Pressure^a

| Alkene | OH yield |
|-----------------------|---------------------------------------|
| Ethene | 0.12 ^b , 0.08 ^b |
| Propene | 0.33 ^a , 0.18 ^b |
| 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 ^b |
| trans-2-Butene | 0.64 ^a , 0.24 ^b |
| 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 ^b -1.0 ^{a,d} |
| Limonene | 0.86 ^b |
| Myrcene | 1.15 ^b |
| α-Pinene | 0.70-0.85 ^{b,e,d} |
| 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} |

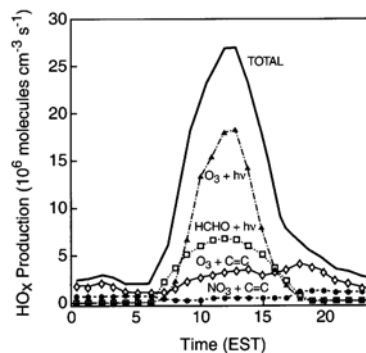


FIGURE 6.6 Calculated rates of HO_x radical generation from various sources for a rural forested site in the southeastern United States (adapted from Paulson and Orlando, 1996).

Specially important at night
because no photolytic OH sources

E

NO₃ + Alkenes

- NO₃ adds to double bond
- Excited adduct can:
 - Form epoxide
 - Stabilize, form peroxy radical, blah blah...

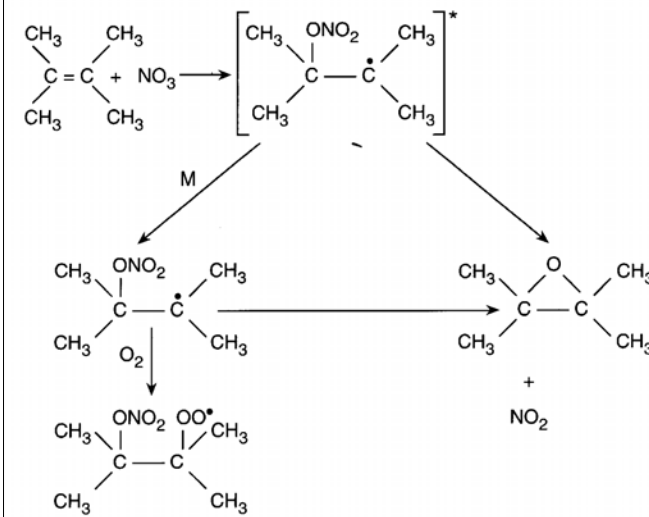


FIGURE 6.8 Mechanism of the NO₃ reaction with 2,3-dimethyl-2-butene (adapted from Skov *et al.*, 1994).

E

NO₃ Reaction Rates

TABLE 6.13 Room Temperature Rate Constants and Gas-Phase Reactions of the NO₃ Radical

- Remember that collision rate $\sim 2.5 \times 10^{10}$
- Reactions are quite fast for biogenic alkenes
 - Comparable rates to OH
- $d[\text{Org}]/dt = -k[\text{Oxidant}][\text{Org}]$
 - NO₃: 50 ppt @ night
 - OH: 0.1 ppt @ day
- NO₃ reactions with biogenic alkenes @ night are very important

| 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} |
| <i>cis</i> -2-Butene | 3.5×10^{-13} |
| <i>trans</i> -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 | $< 6 \times 10^{-16 d}$ |
| Methacrolein | $3.3 \times 10^{-15 e}$ |

Biogenics

F,G,H,I

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

J

Biogenic VOCs

TABLE 6.24 Estimated Global Annual Biogenic VOC Emissions (Tg yr^{-1})^a

| Source | Isoprene | Monoterpenes | Other VOCs ^b |
|---|----------|--------------|-------------------------|
| Canopy foliage | 460 | 115 | 500 |
| Terrestrial ground cover and soils | 40 | 13 | 50 |
| Flowers | 0 | 2 | 2 |
| Ocean and freshwater | 1 | <0.001 | 10 |
| Animals, humans, and insects | 0.003 | <0.001 | 0.003 |
| Anthropogenic (including biomass burning) | 0.01 | 1 | 93 |
| Total | ~500 | ~130 | ~650 |

^a From Guenther (1999) and references therein.

^b Other VOCs include all volatile organic compounds other than methane, isoprene, and monoterpenes.

- Biogenic VOCs dominate globally
- Lots of double bonds...
- Large → products to aerosols



Isoprene

 α -Pinene β -Pinene

Limonene

 α -Terpinene γ -Terpinene

Camphene



Terpinolene

 α -Phellandrene β -Phellandrene

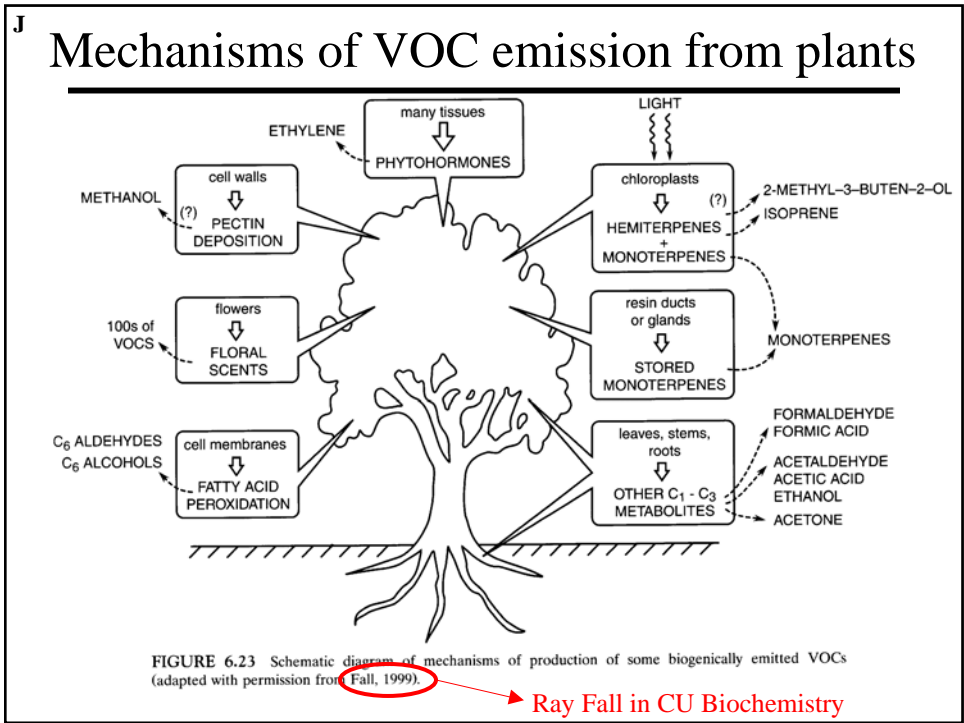
Myrcene



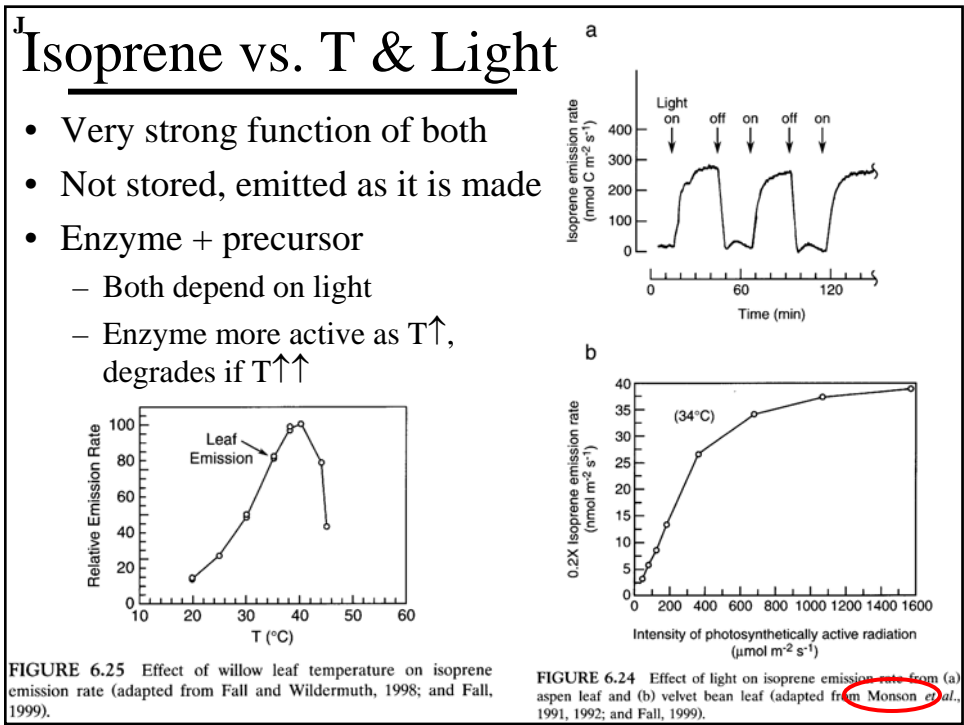
Ocimene

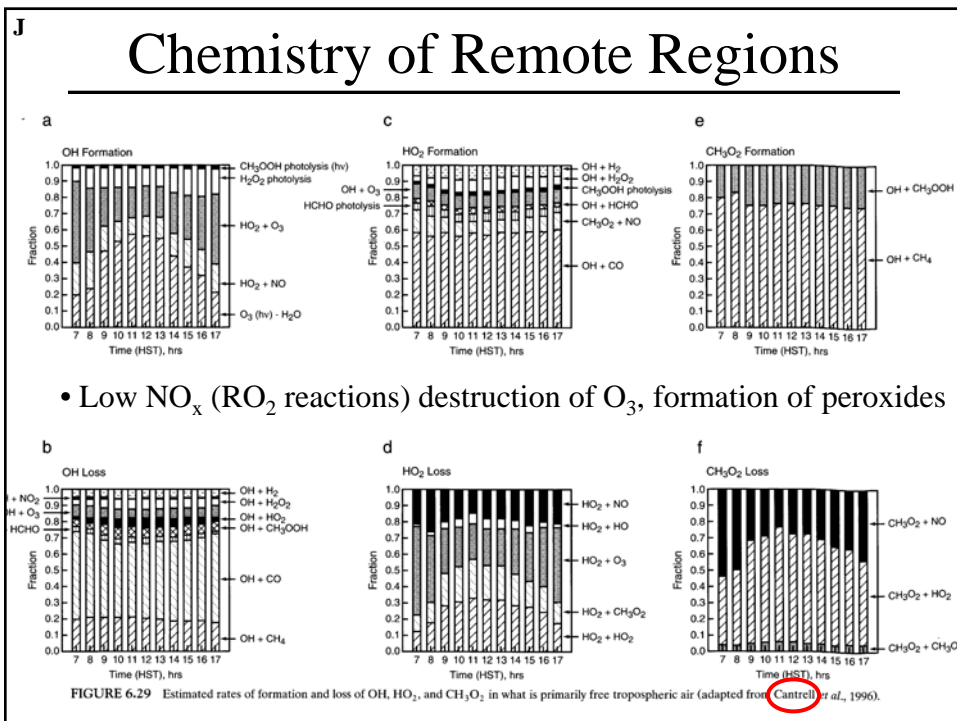
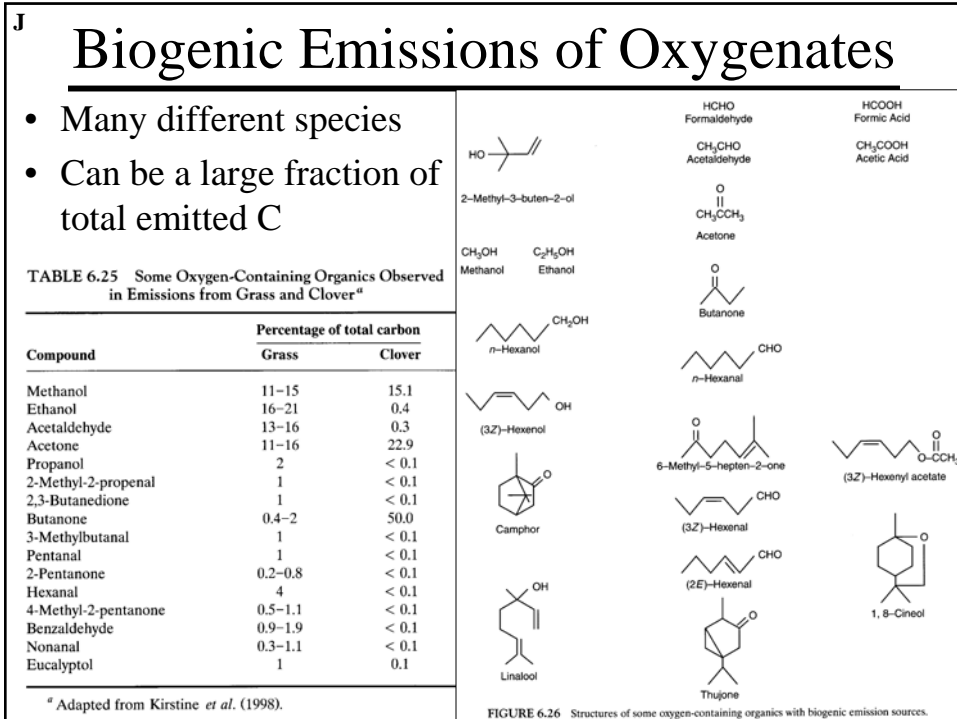
 Δ^3 -Carene*p*-Cymene

FIGURE 6.22 Chemical structures of some biogenically emitted hydrocarbons.



Ray Fall in CU Biochemistry





K Biomass Burning Emissions

TABLE 6.27 Estimated Emissions from Biomass Burning Compared to Global Emissions^a

| Species | Biomass burning (Tg of element / yr) | All sources (Tg of element / yr) | Biomass burning (%) |
|---|--------------------------------------|----------------------------------|---------------------|
| Carbon dioxide (gross from combustion) | 3500 | 8700 | 40 |
| Carbon dioxide (net from deforestation) | 1800 | 7000 | 26 |
| Carbon monoxide | 350 | 1100 | 32 |
| Methane | 38 | 380 | 10 |
| Nonmethane hydrocarbons ^b | 24 | 100 | 24 |
| Nitrous oxide | 0.8 | 13 | 6 |
| NO _x | 8.5 | 40 | 21 |
| Ammonia | 5.3 | 44 | 12 |
| Nitrous oxide | 0.8 | 13 | 6 |
| Sulfur gases | 2.8 | 150 | 2 |
| Carbonyl sulfide | 0.09 | 1.4 | 6 |
| Methyl chloride | 0.51 | 2.3 | 22 |
| Hydrogen | 19 | 75 | 25 |
| Tropospheric ozone ^c | 420 | 1100 | 38 |
| Total particulate matter | 104 | 1530 | 7 |
| Particulate organic carbon | 69 | 180 | 39 |
| Elemental carbon (black soot) | 19 | <22 | >86 |

^a From Andreae (1991); see for original references.

^b Excluding isoprene and terpenes.

^c Formed from reactions in air due to biomass burning.

- Very important source of many species
- Being studied intensively (NCAR)

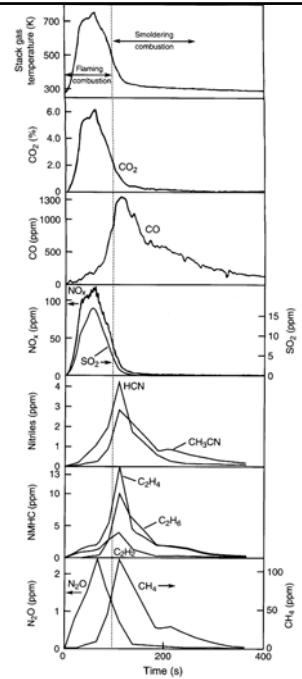


FIGURE 6-40 Stack gas temperature and emissions of various species from an experimental burning of grass in Venezuela (adapted from Critzer and Andreae, 1990).