Atmos. Chem. Lecture 12, 10/21/13: Atmospheric organic chemistry (intro!)

Jareth: Measurement networks

OH + alkanes: New branch points

Other oxidants, hydrocarbons

Implications for HO_x

PSet 3 due Wed 10/23; Midterm Wed 10/30

Review: HO_x, NO_x, CO, CH_4

Wofsy et al., "Atmospheric CH_4, CO, and CO_2", *JGR* 77:4477 (1972)
Logan et al., "Tropospheric Chemistry: A Global Perspective", *JGR* 86:7210 (1981)

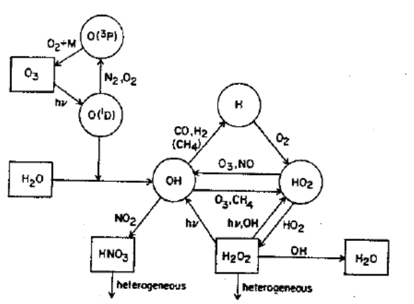


Fig. 1. Major chemical reactions affecting odd hydrogen (OH, H, HO_2, H_2O_2) in the troposphere.

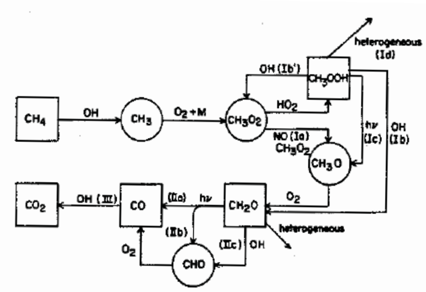


Fig. 2. The atmospheric oxidation of methane.

For more info on complex organics…

Books:

S&P section 6.10; Finlayson-Pitts and Pitts, Ch. 6

Calvert et al., *Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford, 2000

Calvert et al., *Mechanisms of Atmospheric Oxidation of the Aromatic Hydrocarbons*, Oxford, 2002

Calvert et al., *Mechanisms of Atmospheric Oxidation of the Oxygenates*, Oxford, 2011

Calvert et al.,

Journal Articles:

Atkinson and Arey, "Atmospheric Degradation of Volatile Organic Compounds", *Chem. Rev.*, 103:4605 (2003)

Atkinson and Arey, "Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review", *Atmos. Environ.*, 37:S197 (2003)

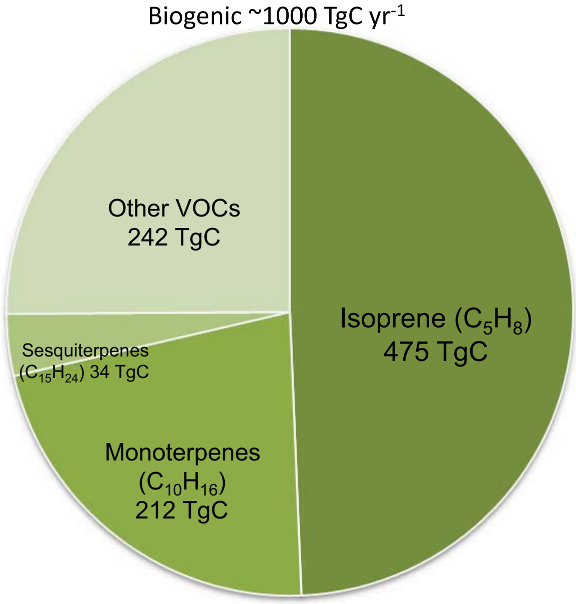
Mellouki et al. "Kinetics and Mechanisms of the Oxidation of Oxygenated Organic Compounds in the Gas Phase", *Chem. Rev.* 103:5077 (2003)

Orlando et al., "The Atmospheric Chemistry of Alkoxy Radicals", *Chem. Rev.* 103:4657 (2003)

Tyndall et al., "Atmospheric chemistry of small organic peroxy radicals", *JGR* 106:12157 (2001)

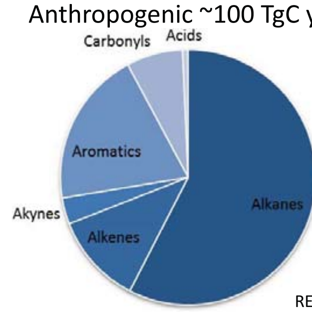
Global non-methane VOC emissions

Biogenic ~1000 TgC yr^{-1}



MEGAN 2.1, Year 2000
Guenther et al., *GMDD* 5:1503, 2012

Anthropogenic ~100 TgC yr^{-1}



RETRO inventory

Biomass Burning
~500 Tg yr^{-1}

Yokelson et al., *ACP* 8:3509 (2008)

OH + alkanes

Analogous to methane oxidation (with some important differences!)

$$CH_4 \xrightarrow{OH} CH_3 \xrightarrow{O_2} CH_3O_2 \xrightarrow{NO} CH_3O \xrightarrow{O_2} CH_2O$$

$$CH_3O_2 \xrightarrow{HO_2} CH_3OOH$$

[Note: Additional material is discussed here during lecture.]

Organic nitrates

$$RO_2 + NO \rightarrow OONO \rightarrow O + NO_2$$
$$\rightarrow ONO_2$$

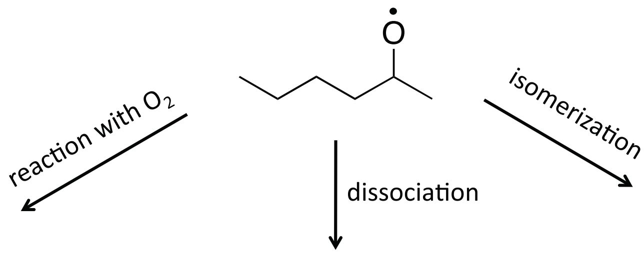
TABLE 6.5 Yields of $RONO_2$ in RO_2 + NO Reactions at Room Temperature and 1 atm[a]

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
n-Hexane	
1-Hexyl	0.12
2-Hexyl	0.22[b]
3-Hexyl	0.22[b]
2-Methylpentane	
2-Methyl-2-pentyl	0.035
3-Methylpentane	
3-Methyl-2-pentyl	0.14–0.16
n-Heptane	
1-Heptyl	0.20
2-Heptyl	0.32[b]
3-Heptyl	0.31[b]
4-Heptyl	0.29[b]
n-Octane	
1-Octyl	0.36
2-Octyl	0.35[b]
3-Octyl	0.34[b]
4-Octyl	0.32[b]

[a] Adapted from Lightfoot *et al.* (1992).

FP&P

Alkoxy radicals: Branching



[Note: Additional material is discussed here during lecture.]

Fate of alkoxy radicals

TABLE 6.7 Rates (s^{-1}) of Alkoxy Radical Reactions at 298 K and 1 atm Air[a]

RO	Decomposition	Reaction with O_2[b]	Isomerization
$CH_3O\cdot$	5.3×10^{-2}	1×10^4	
$C_2H_5O\cdot$	0.3	5×10^4	
n-$C_4H_9O\cdot$	5.8×10^2	5×10^4	2.0×10^5
$CH_3-CH(O\cdot)-CH_2CH_3$	2.3×10^4	4×10^4	
$(CH_3)_3CO\cdot$	1×10^3		
$CH_3-CH(O\cdot)-CH_2CH_2CH_3$	1.7×10^4	4×10^4	2×10^5
$CH_3CH_2-CH(O\cdot)-CH_2CH_3$	1.6×10^4	4×10^4	
$CH_3-CH(O\cdot)-(CH_2)_3CH_3$	2.8×10^4	4×10^4	2×10^6
$CH_3CH_2-CH(O\cdot)-(CH_2)_2CH_3$	3.4×10^4	4×10^4	2×10^5
$(CH_3)_3COCH_2O\cdot$	1.1×10^{-3}	3.8×10^6	2.0×10^5
$CH_3-C(CH_3)_2-CH_2O\cdot$	9.8×10^3	2.4×10^4	$\geq 7 \times 10^4$

[a] Adapted from Atkinson (1994, 1997a, 1997b) and Atkinson *et al.* (1995b).
[b] Shown as $k[O_2]$ (s^{-1}), based on recommended rate constants for RO + O_2 (Atkinson, 1997a).

Also see :
- Orlando et al., Chem Rev. 103:4657 (2003)
- Atkinson, *Atmos. Environ.* 41:8468 (2007)
- Kroll and Seinfeld, *Atmos. Environ.* 42:3593 (2008)

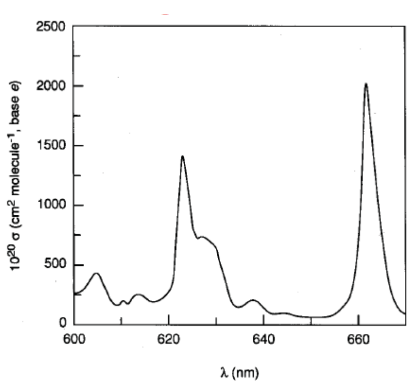
FP&P

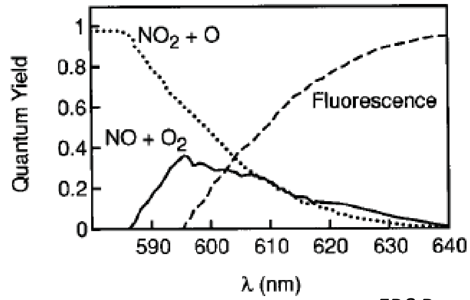
Tropospheric oxidants

Images removed due to copyright restrictions. See Table 6.1 in Finlayson-Pitts and Pitts, *Chemistry of the Upper and Lower Atmosphere*. Academic Press, 2000.

NO_3 formation, photolysis

NO_2 + hv → NO + O
$NO_2 + O_3$ → $NO_3 + O_2$
NO_3 + hv → NO_2 + O
→ NO + O_2
$NO_3 + NO_2$ + M → N_2O_5 + M
NO_3 + NO → $2NO_2$
NO_3 + org → products





FP&P

Chlorine chemistry

$$N_2O_5(g) + NaCl \rightarrow ClNO_2\,(g) + NaNO_3$$
$$ClNO_2 + h\nu \rightarrow Cl + NO_2$$

$$ClONO_2(g) + NaCl \rightarrow Cl_2\,(g) + NaNO_3$$
$$Cl_2 + h\nu \rightarrow Cl + Cl$$

A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry

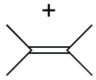
Joel A. Thornton[1], James P. Kercher[1]†, Theran P. Riedel[1,2], Nicholas L. Wagner[3], Julie Cozic[3,4], John S. Holloway[3,4], William P. Dubé[3,4], Glenn M. Wolfe[1,2], Patricia K. Quinn[5], Ann M. Middlebrook[3], Becky Alexander[1] & Steven S. Brown[3]

Nature 464:271 (2010)

Oxidants + alkenes

OH

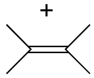
+



k ≅ 10^{-11}-3×10^{-10} cm^3 $molec^{-1}$ s^{-1}

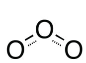
NO_3

+

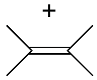


k ≅ 10^{-14}-10^{-11} cm^3 $molec^{-1}$ s^{-1}

[Note: Additional material is discussed here during lecture.]

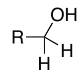


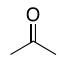
+

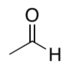


k ≅ 10^{-18}-10^{-14} cm^3 $molec^{-1}$ s^{-1}

OH + simple oxygenates

alcohols OH + 

ketones OH + 

aldehydes OH + 

etc.

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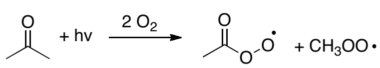
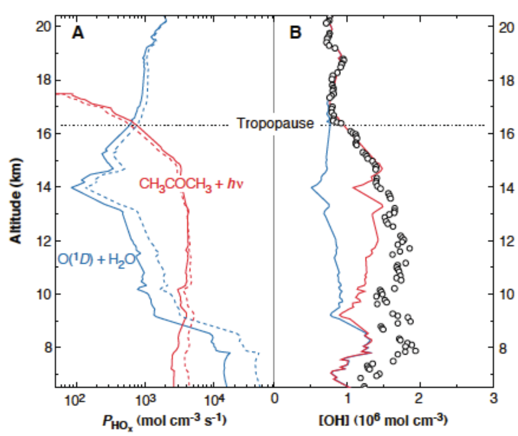
Acetone photolysis

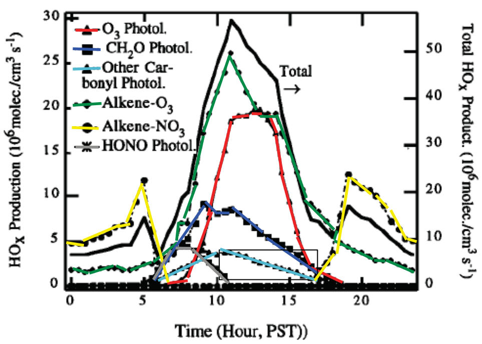




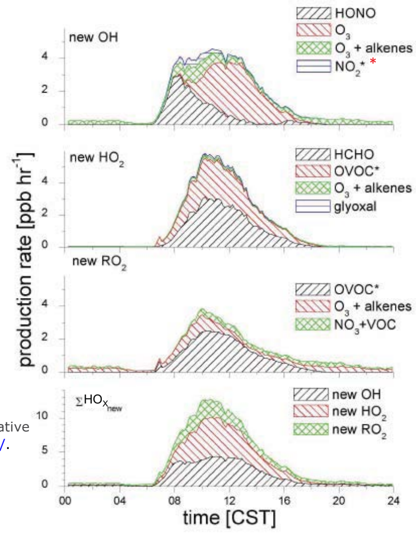
Wennberg et al., *Science* 279:49 (1998)

[Note: Additional material is discussed here during lecture.]

Additional HO_x sources (urban)



Paulson and Orlando, *GRL* 23:3727 (1996)

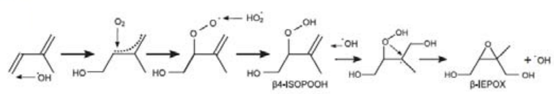


Volkamer et al., ACP 10:6969 (2010)

* Li et al, Science 319:1657 (2008)

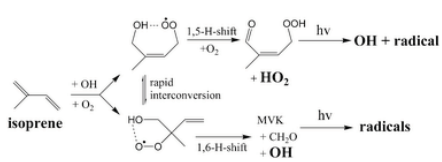
Complex (functionalized) organics: New chemistry

Unimolecular alkyl (R) radical chemistry

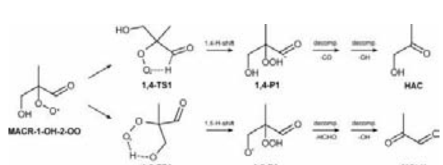


Paulot et al., *Science* 325:730 (2009)
Kjaergaard et al., *J. Phys. Chem. A* 116:5763 (2012)

Unimolecular alkylperoxy (RO_2) radical chemistry



Peeters et al. *PCCP*, 11:5935 (2009)
Crounse et al., *PCCP*, 13:13607 (2011)



Crounse et al., *J. Phys. Chem A*, 116:5756 (2012)
Crounse et al., *J. Phys. Chem Lett*, 4:3513 (2013)

Chemistry of other species: organic peroxides, nitrates, acids?...

1.84J / 10.817J / 12.807J Atmospheric Chemistry
Fall 2013