

# Studies of the Atmospheric Chemistry of Volatile Organic Compounds and of their Atmospheric Reaction Products

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# VOC Chemistry Studied

- Alkanes, including of their first-generation products.
- Alkenes.
- Nitro-PAH formation and presence in ambient air.
- Oxygenated VOCs: alcohols, diols, and aldehydes.

# In the troposphere, VOCs are chemically removed by:

- Photolysis at wavelengths  $>290$  nm.
- Reaction with the hydroxyl (OH) radical, mainly during daylight hours.
- Reaction with the nitrate ( $\text{NO}_3$ ) radical during evening and nighttime hours.
- Reaction with ozone ( $\text{O}_3$ ).

# O<sub>3</sub> in the troposphere

- O<sub>3</sub> is transported down from the stratosphere, with deposition at the Earth's surface.
- O<sub>3</sub> is produced *in situ* in the troposphere from the oxidation of VOCs in the presence of NO - a prime example being in urban areas!

# OH radicals in the troposphere

- From the photolysis of O<sub>3</sub>:



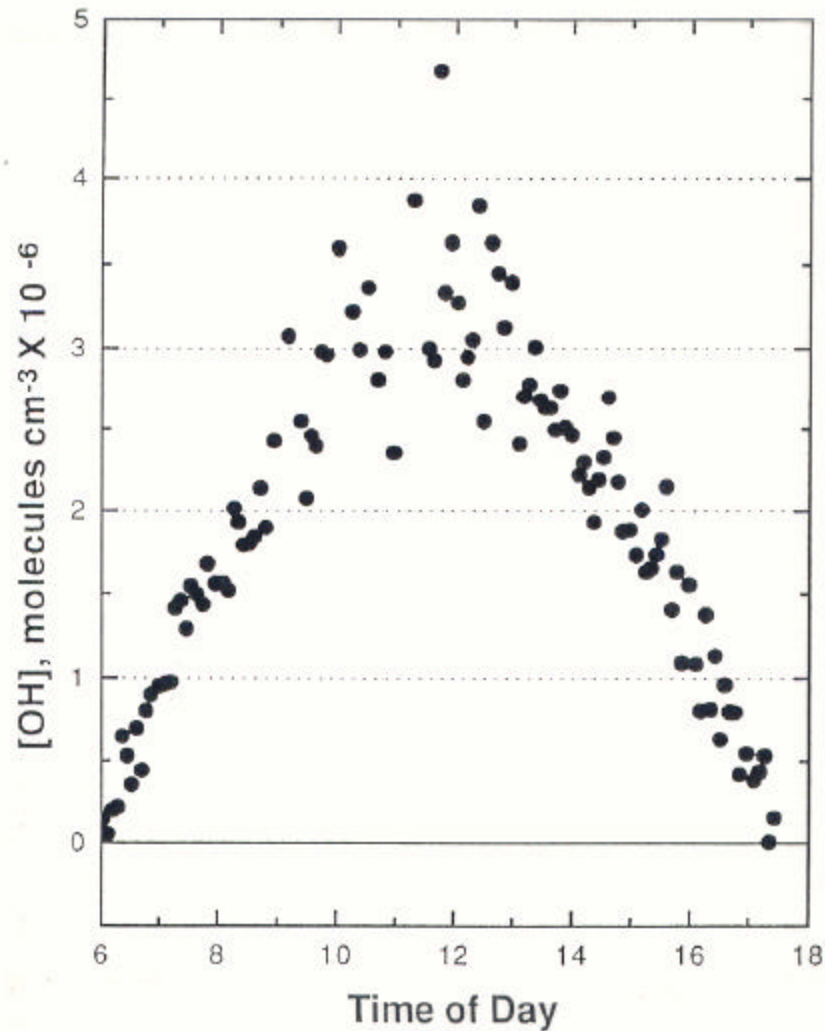
- From the photolysis of nitrous acid



# OH radicals (cont.)

- From the photolysis of formaldehyde





OH radical concentrations measured on September 21, 1993, in Colorado (Tanner *et al.*, 1997)

# NO<sub>3</sub> radicals in the troposphere

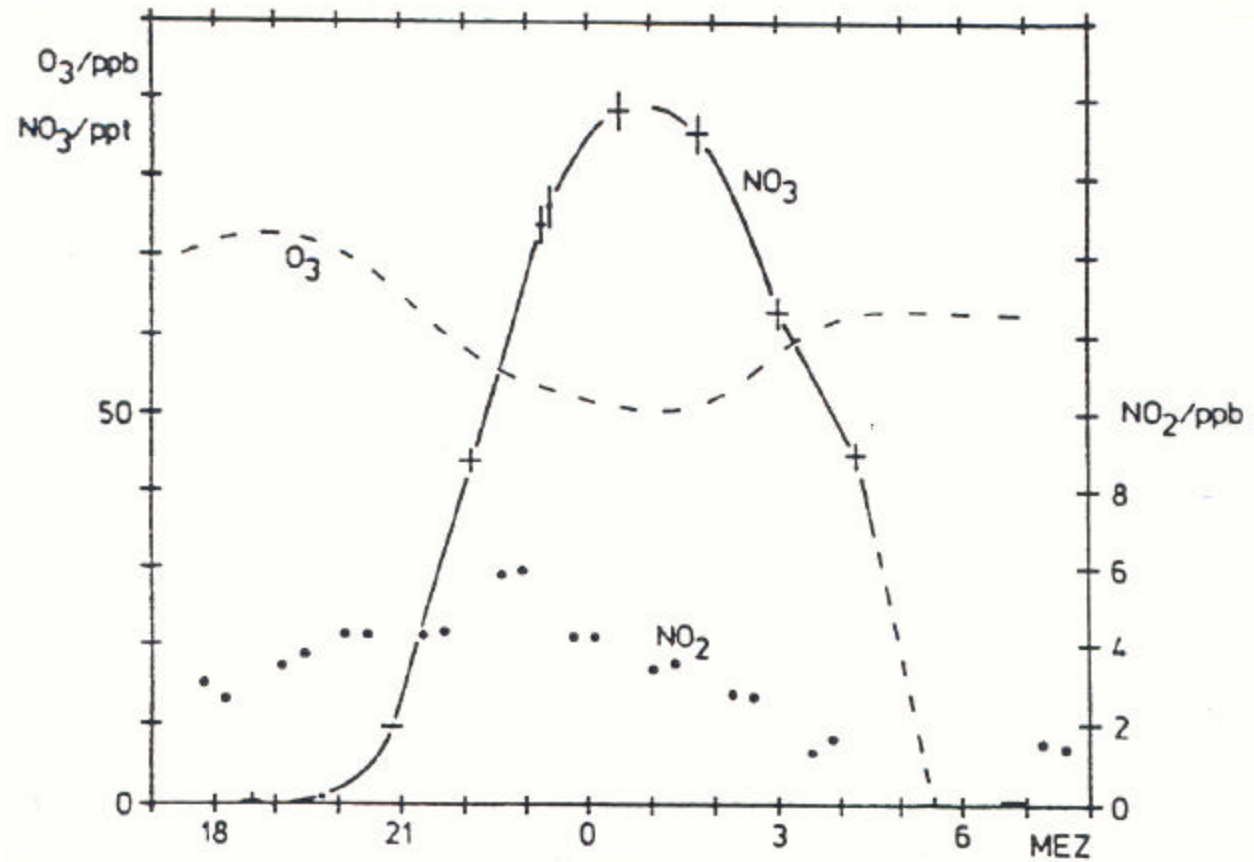
- Formed by:



and removed by rapid photolysis and reaction with NO.

- Hence NO<sub>3</sub> radicals are observed during late evening and nighttime hours.





$\text{NO}_3$  radical mixing ratio at Deuselbach, Germany, July 7/8, 1983 (Platt and Hausmann, 1994)

# Experimental Methods

- Experiments were carried out in large volume (5800-7500 liter) chambers.
- OH radicals were generated by photolysis of methyl nitrite in air:



- O<sub>3</sub> was generated using a commercial ozone generator. Cyclohexane or 2-butanol were added at concentration sufficient to scavenge >95% of the OH radicals formed in O<sub>3</sub> + alkene reactions.
- NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>:



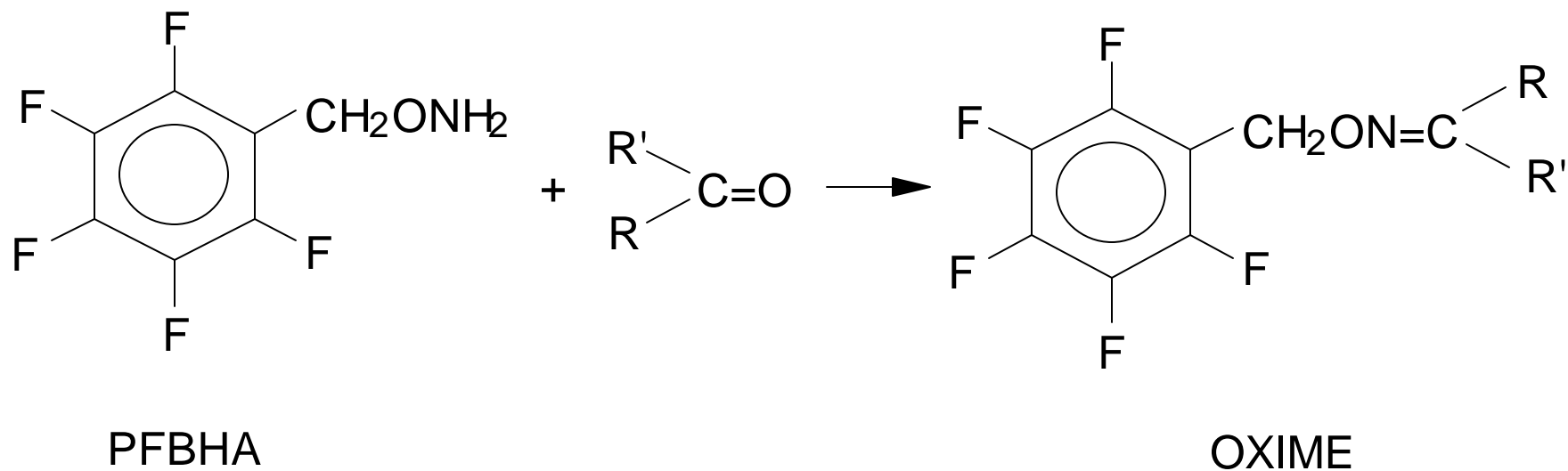
- Initial concentrations (in molecule  $\text{cm}^{-3}$ ) depended on the analytical technique used, and for GC analyses were typically:
  - VOC(s),  $2.4 \times 10^{13}$
  - $\text{CH}_3\text{ONO}$  and  $\text{NO}$ ,  $2.4 \times 10^{14}$  each, or  $\text{O}_3$ ,  $5 \times 10^{12}$  per addition
  - For *in situ* FT-IR analyses, VOC and  $\text{O}_3$  concentrations were a factor of  $\sim 10$  higher, and  $\text{N}_2\text{O}_5$  concentrations were  $\sim 1 \times 10^{14}$  per addition.

# Analytical techniques

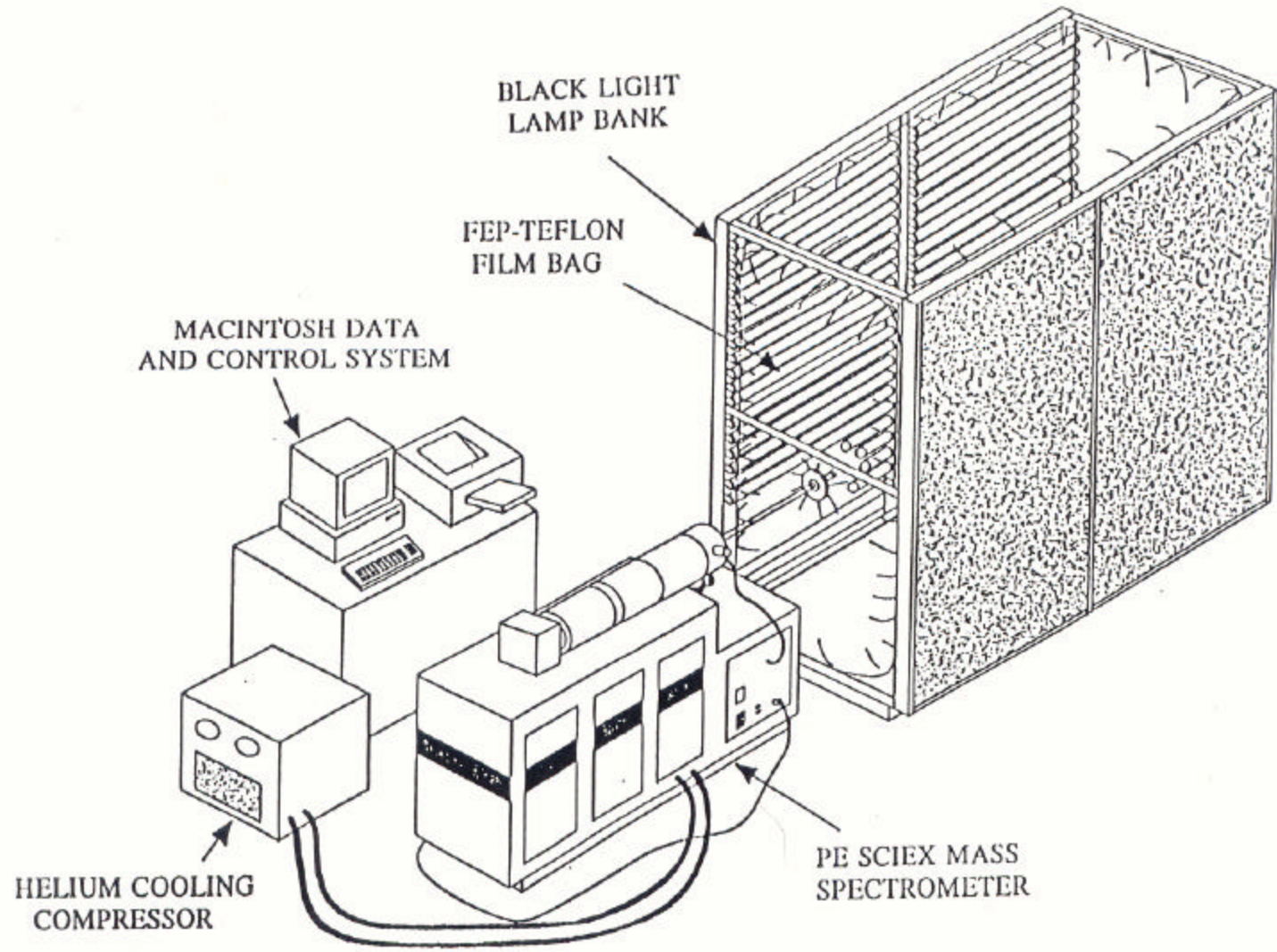
- GC-FID and GC-MS, with typically 100 cm<sup>3</sup> volume samples collected onto Tenax solid adsorbent with subsequent thermal desorption onto the GC column.
- Use of Solid Phase MicroExtraction fibers (SPME) with GC-FID and GC-MS.
- *In situ* API-MS and API-MS/MS.
- *In situ* FT-IR spectroscopy.

# Solid Phase MicroExtraction (SPME) fibers

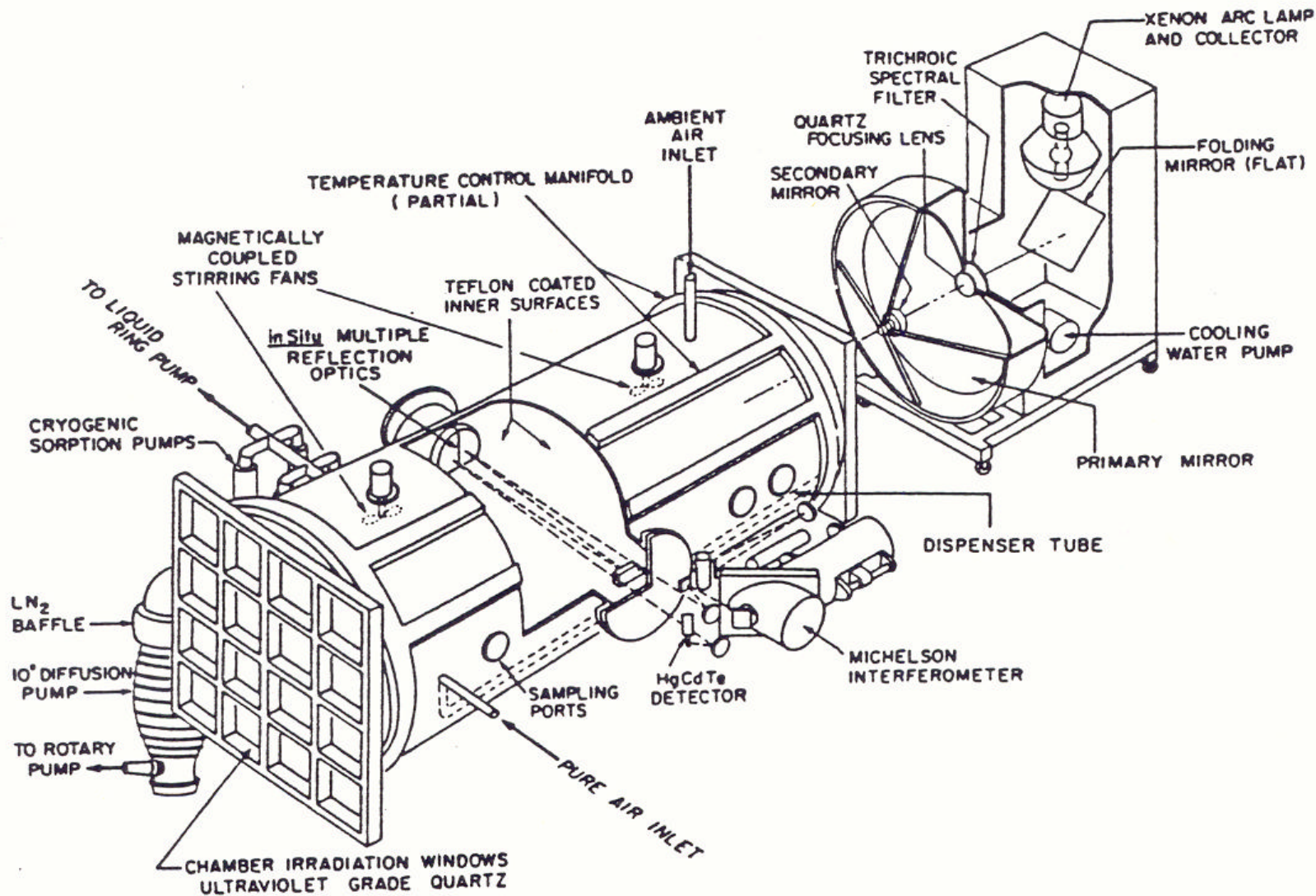
- Fiber coated with GC column phase. VOCs partition between fiber coating and gas phase.
- Fibers were pre-coated with a derivatizing agent, *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) hydrochloride for the analysis of carbonyl-containing compounds.



Oximes may be formed as the *Z*- and *E*- isomers





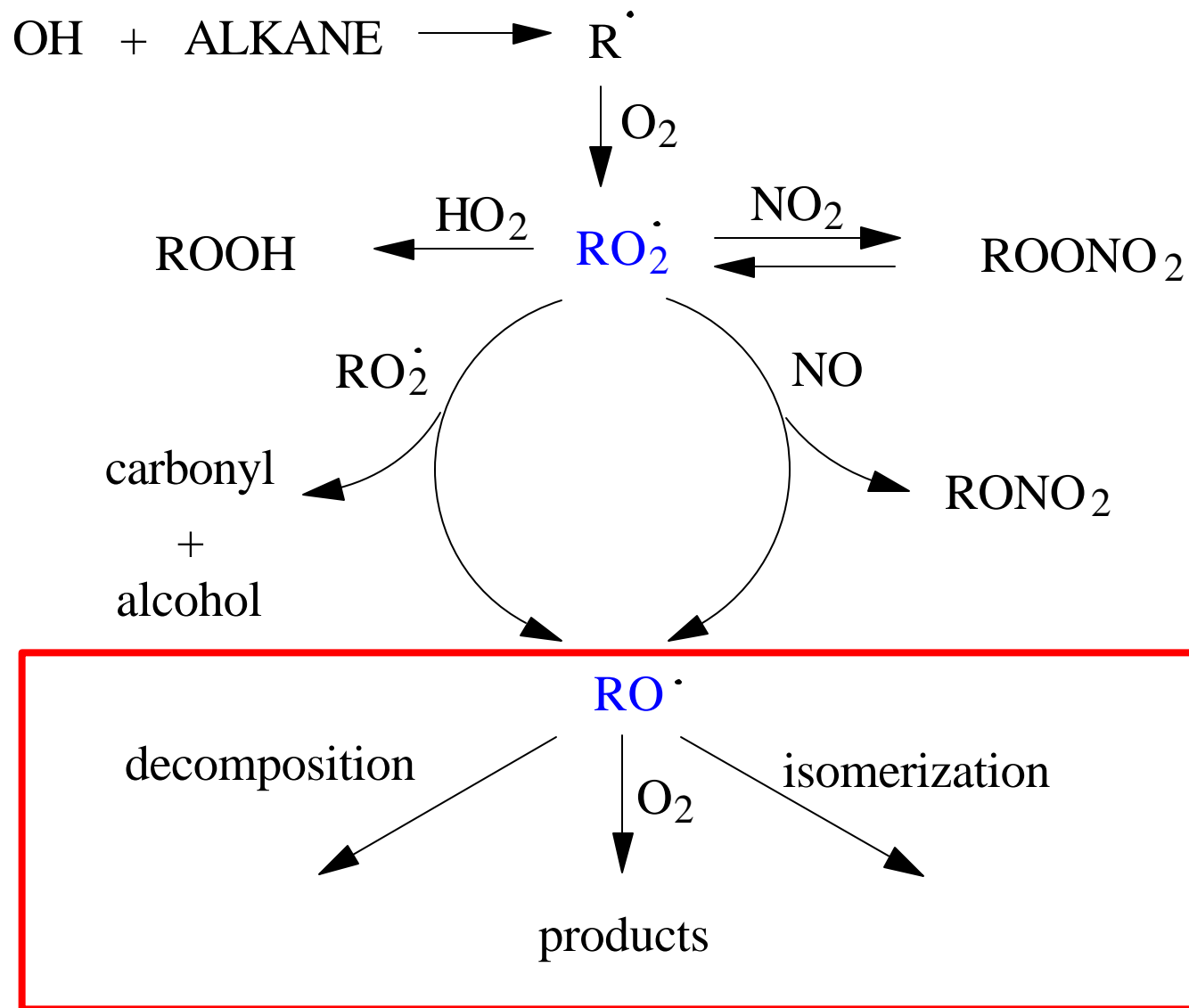


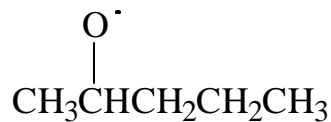
# Alkane Chemistry

(React with OH radicals)

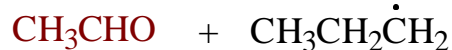
# Studies of Alkane Chemistry

- OH + 2,2,4- and 2,3,4-trimethylpentane in the presence of NO.
- Identification of 1,4-hydroxycarbonyls from OH + *n*-pentane through *n*-octane.
- Atmospheric chemistry of 5-hydroxy-2-pentanone.
- Formation of 2,3-dihydro-2-methylfuran from 5-hydroxy-2-pentanone and its reactions.





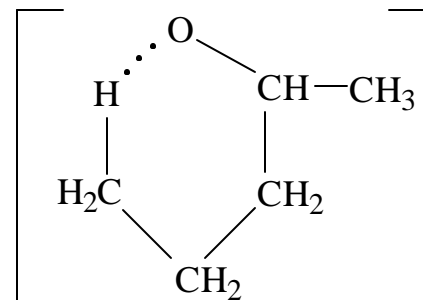
decomposition



$\text{O}_2$



isomerization

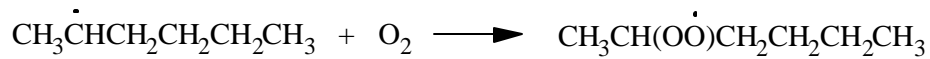


and



More important for more highly branched alkanes

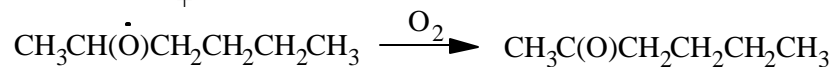
More important for longer alkanes



NO



NO<sub>2</sub>

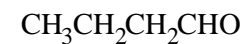


isomerization

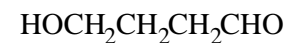
decomposition



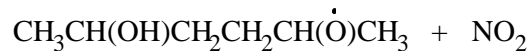
O<sub>2</sub>



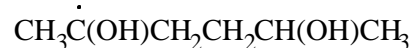
and



NO



isomerization



O<sub>2</sub>



# Product distributions for selected alkanes

alkane	carbonyls (O <sub>2</sub> react.)	carbonyls (decomp.)	hydroxy- carbonyls
<i>n</i> -butane (8% nitrate)	57%	26%	9%
<i>n</i> -octane (28% nitrate)	<1%	<1%	~52%
2,3,4-TMP		55-70%	10-15%

# OH + Alkane Products

- In the presence of NO, products formed are alkyl nitrates, carbonyls (from alkoxy decomposition and reaction with O<sub>2</sub>), and hydroxynitrates and hydroxycarbonyls (from alkoxy radical isomerization).
- Alkoxy decomposition becomes more important for branched alkanes.
- If alkoxy isomerization can occur, it dominates over the O<sub>2</sub> reaction, and competes with alkoxy decomposition in branched alkanes.



# Observed products (molar %)

alkane	nitrate	carbonyl	hydroxy-nitrate	hydroxy-carbonyl
<i>n</i> -pentane	10.5	50	2.5	54
<i>n</i> -hexane	14.1	10	4.5	57
<i>n</i> -heptane	17.8	<1	4.6	51
<i>n</i> -octane	22.6	<1	5.3	53

# Identification of 1,4-hydroxycarbonyls from OH + alkanes

- We used SPME fibers pre-coated with PFBHA to collect carbonyl products of the reactions of OH radicals with *n*-pentane through *n*-octane, with thermal desorption/GC-MS analyses.
- Hydroxycarbonyls identified from mass spectra, including fragmentation patterns.
- 5-Hydroxy-2-pentanone (formed from *n*-pentane) is commercially available.

Hydroxycarbonyls from  
OH + *n*-hexane;  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

- 4-Hydroxyhexanal (**minor**)



- 5-Hydroxy-2-hexanone



- 6-Hydroxy-3-hexanone



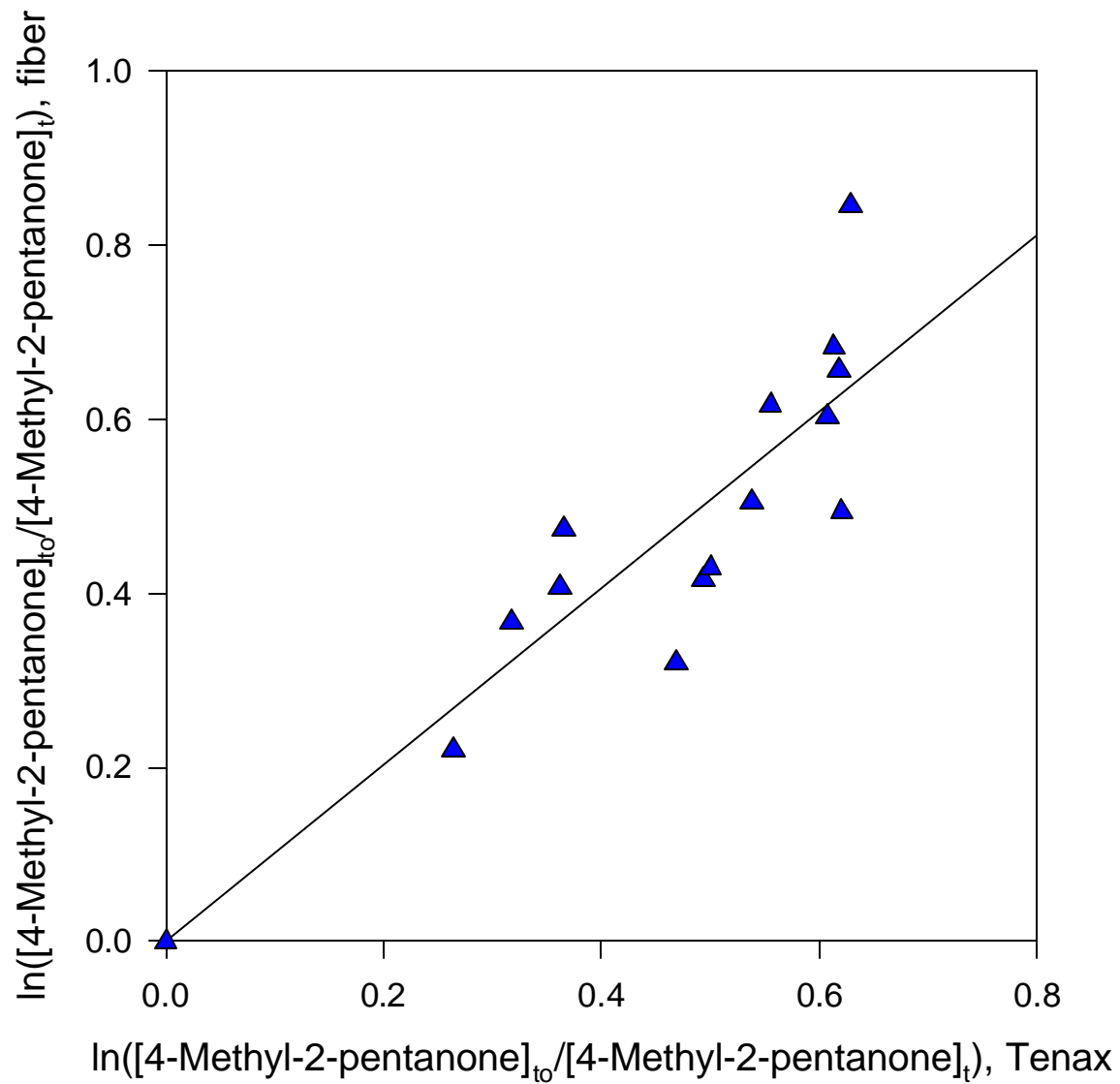
# Observed products (molar %)

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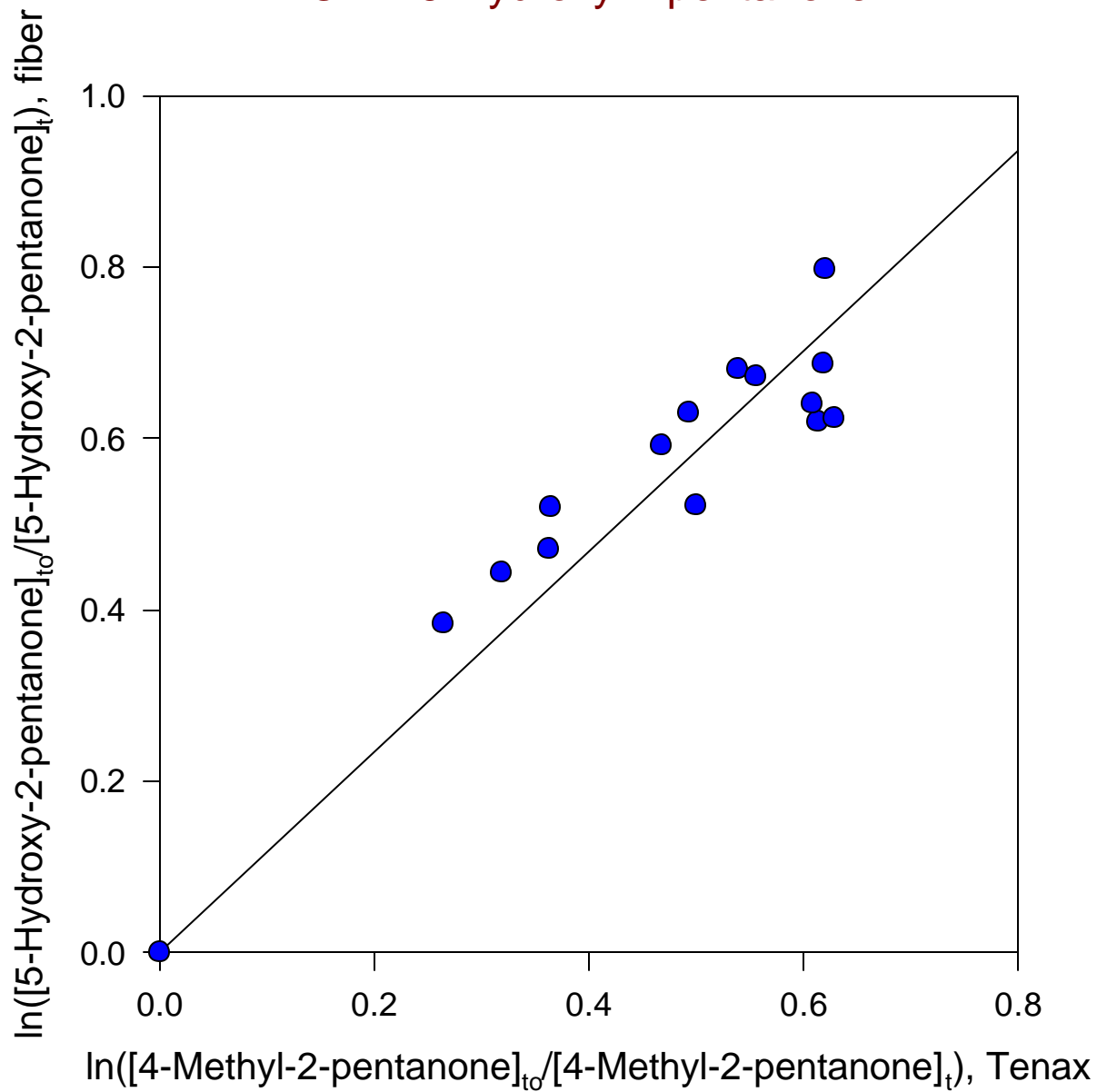
# Atmospheric chemistry of 5-hydroxy-2-pentanone

- The only commercially available 1,4-hydroxycarbonyl. Does not elute from GC column without prior derivatization. We analyzed 5-hydroxy-2-pentanone by GC-FID as its oxime after collection on a SPME fiber coated with PFBHA.

OH + 4-Methyl-2-pentanone; analyses by  
GC-FID (Tenax) and GC-FID (SPME)



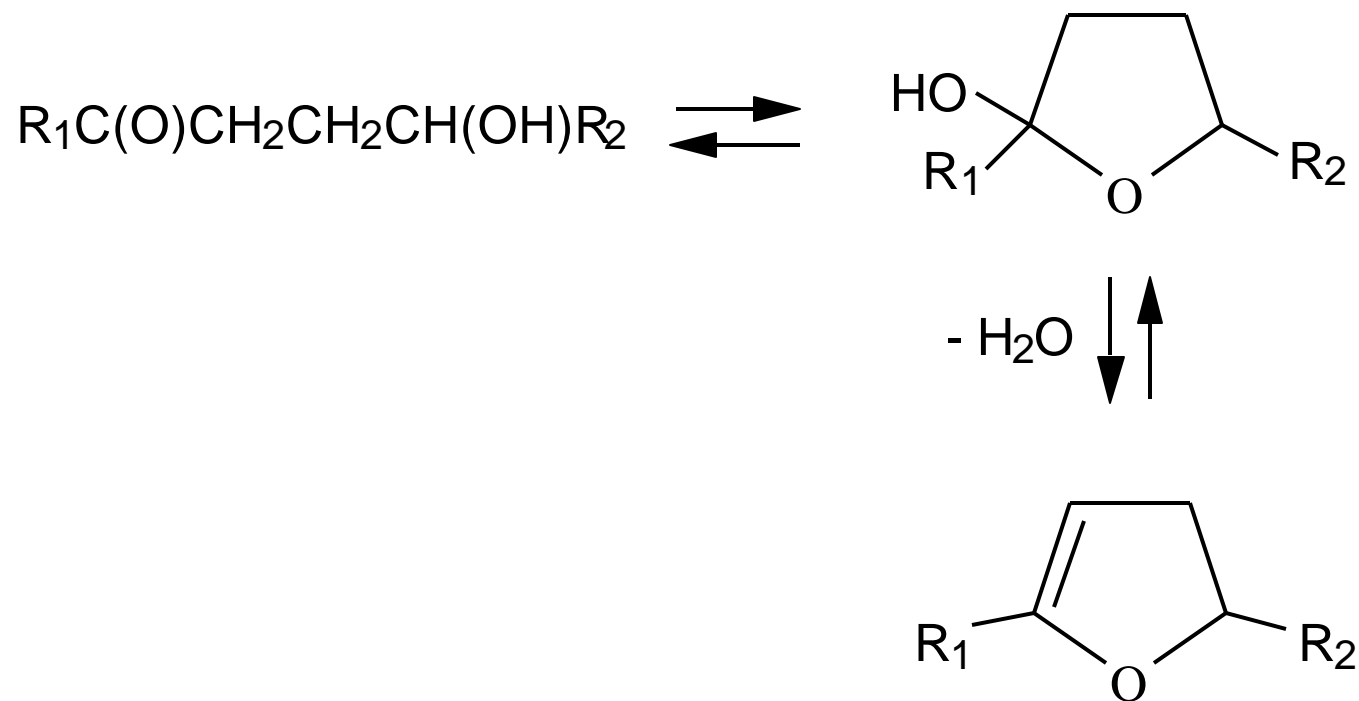
# OH + 5-Hydroxy-2-pentanone



# Dark reactions

- In dry air, 5-hydroxy-2-pentanone decayed, with a lifetime of  $\sim 1$  hr, to form 4,5-dihydro-2-methylfuran.
- At 5% relative humidity, 4,5-dihydro-2-methylfuran decayed, with a lifetime of  $\sim 3.5$  hr, to form 5-hydroxy-2-pentanone.





Recent work indicates that for larger hydroxy-carbonyls, conversion to the dihydrofurans is still important up to 50% relative humidity.

# Reactions of 4,5-dihydro-2-methylfuran

- Reacts very rapidly with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub>. Daytime lifetimes:

<i>n</i> -Pentane:	36 hr
5-Hydroxy-2-pentanone:	9 hr
4,5-Dihydro-2-methylfuran:	0.6 hr

# Alkene Chemistry

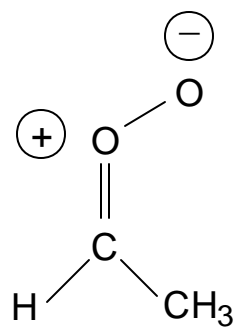
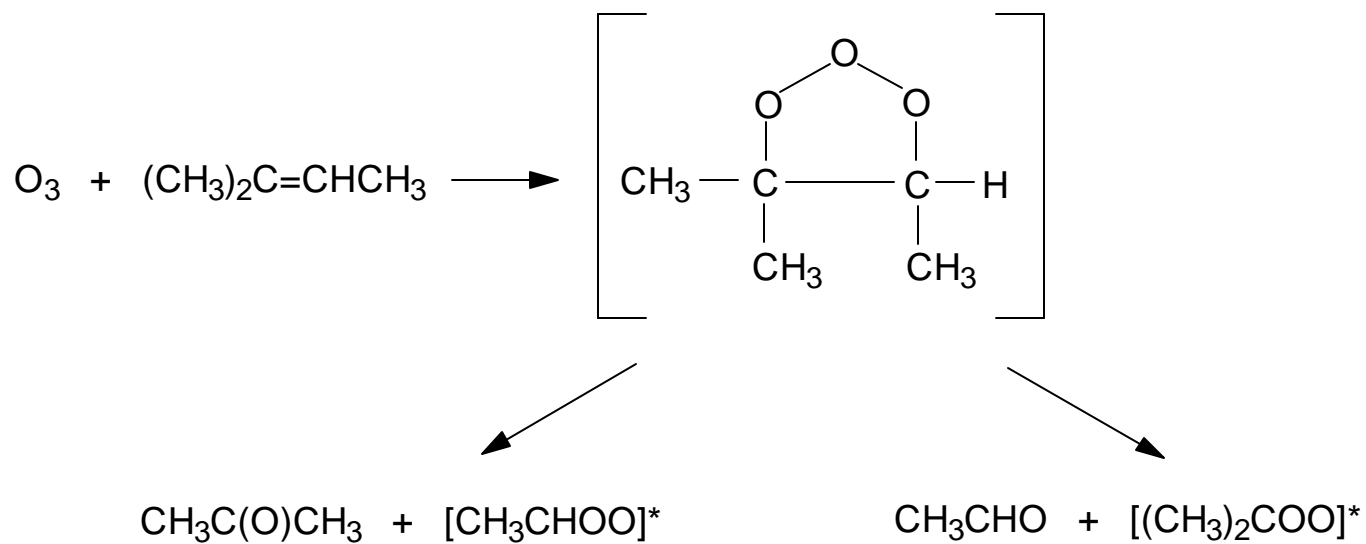
(react with OH radicals, NO<sub>3</sub> radicals and O<sub>3</sub>)

# Studies of Alkene Chemistry

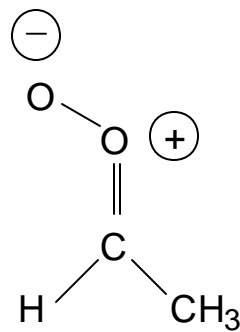
- Investigated the products of the reactions of  $O_3$  with cyclohexene and cyclohexene- $d_{10}$ .
- Analyses were by GC, *in situ* API-MS and *in situ* FT-IR spectroscopy.
- Used cyclohexane and cyclohexene- $d_{12}$  as OH radical scavengers, allowing the products from OH + cyclohexane to be differentiated from those from  $O_3$  + cyclohexene by API-MS and API-MS/MS.

- Studied the effects of varying the water vapor and 2-butanol concentrations on OH radical and selected carbonyl yields from the reactions of O<sub>3</sub> with:

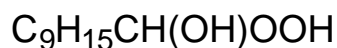
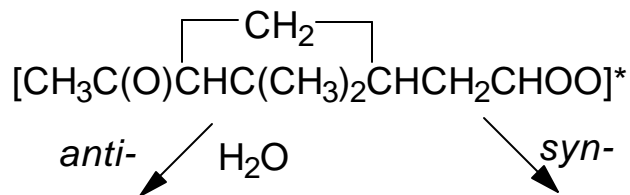
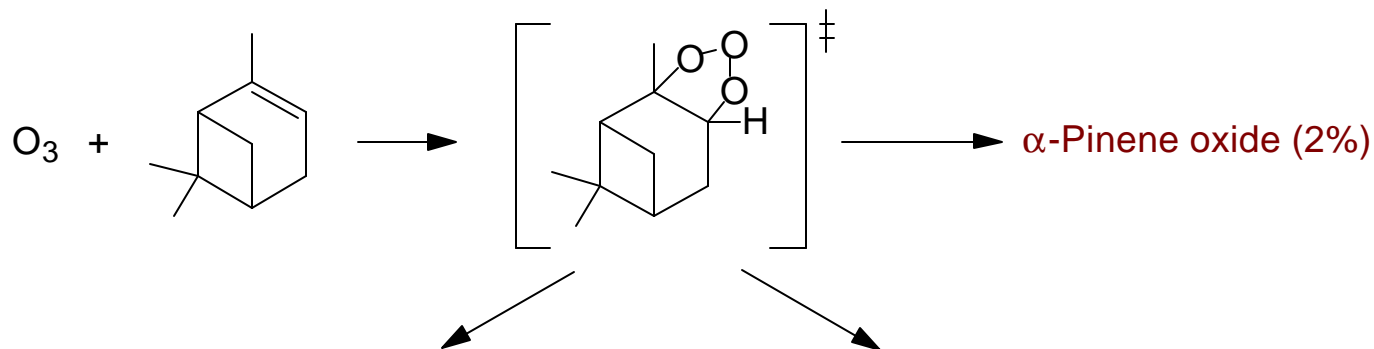
- 1-octene (heptanal)
- *trans*-7-tetradecene (heptanal)
- sabinene (sabinaketone)
- α-pinene (pinonaldehyde)



*syn*

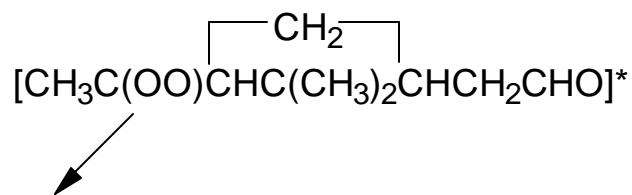


*anti*



16 + 3%

independent of water vapor



**OH**  
80 + 10%

independent of water vapor

+ products including:  $C_{10}$  hydroxydicarbonyl

$C_{10}$  tricarbonyl

$C_{10}$  hydroperoxydicarbonyl

$C_9$  dicarbonyl

# Studies of PAH Chemistry

Methyl- and Dimethyl-/Ethyl-  
Nitronaphthalenes Measured in Ambient  
Air in Southern California



Compared nitro-PAHs in ambient air with  
nitro-PAHs formed from reactions of  
volatilized diesel fuel.

Why nitro-PAHs?

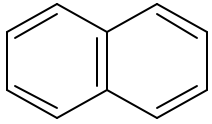
Nitro-PAHs are  
genotoxic.

Why reactions of volatilized diesel  
fuel PAHs?

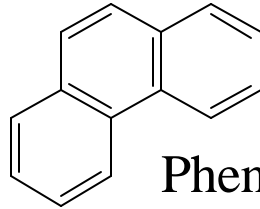
# Gas-phase



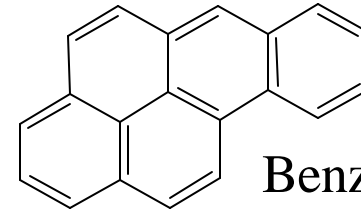
# Particle-associated



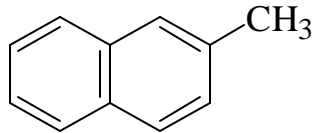
Naphthalene  
0.08 Torr  
1600 ng/m<sup>3</sup>



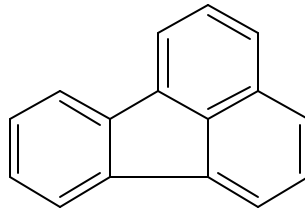
Phenanthrene  
 $1.2 \times 10^{-4}$  Torr  
17 ng/m<sup>3</sup>



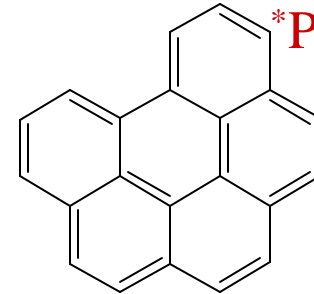
Benzo[a]pyrene\*  
ac 0.2 ng/m<sup>3</sup>  
uf 0.6 ng/m<sup>3</sup>



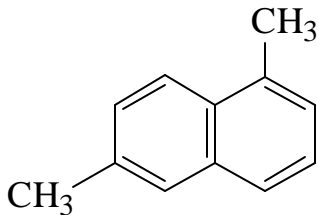
2-MN 730 ng/m<sup>3</sup>  
 $\Sigma$  MNs 1000 ng/m<sup>3</sup>



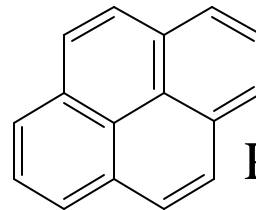
Fluoranthene  
 $9.2 \times 10^{-6}$  Torr  
6.0 ng/m<sup>3</sup>



Benzo[ghi]perylene\*  
ac 0.4 ng/m<sup>3</sup>  
uf 1.5 ng/m<sup>3</sup>  
**\*PM Fine**

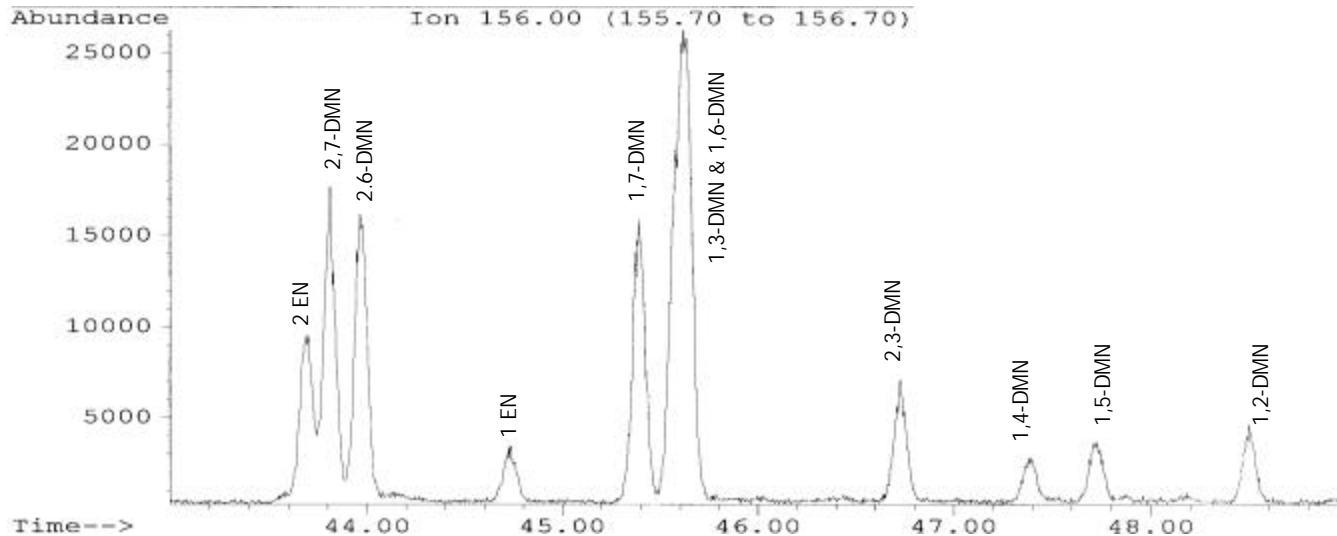
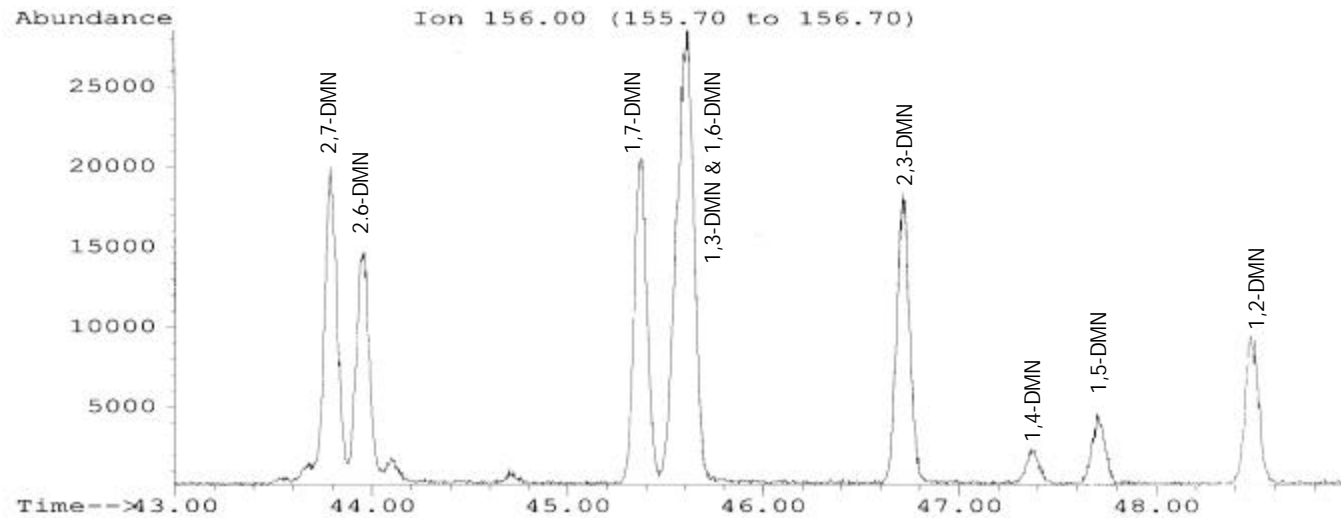


$\Sigma$  DMNs 120 ng/m<sup>3</sup>



Pyrene  
 $4.5 \times 10^{-6}$  Torr  
6.9 ng/m<sup>3</sup>

# GC-MS Chromatogram of C<sub>2</sub>-Naphthalenes



PAH	LA (ng/m <sup>3</sup> ) 7-10:30am	A2 Diesel Fuel (ppm)
Naphthalene	390	1290
1-Methylnaphthalene	170	4040
2-Methylnaphthalene	70	2750
Ratio 2MN/1MN	2.4	1.5
Σ 1 + 2-Ethylnaphth.	6	1670
Σ ENs/ Σ DMNs	0.2	0.15
2,6 + 2,7-DMNs	9 (32%)*	3360 (30%)*
1,3+1,6+1,7-DMNs	14 (51%)*	3630 (32%)*
1,4+1,5+2,3-DMNs	3 (11%)*	2390 (21%)*
1,2-Dimethylnaphth.	2 (6%)*	1870 (17%)*

\* Percent of total dimethylnaphthalenes.

## Naphthalene emissions in the South Coast Air Basin\*

	Emission Rates (kg day <sup>-1</sup> )	Percent of Total
Gasoline exhaust & evap.	745	44%
Diesel engine exhaust	160	9%
Slow cure asphalt	230	13%
Consumer products	254	15%
Mineral spirit & industrial	331	19%

\* Lu et al. (2004).

# EXPERIMENTAL

- Column chromatography to isolate PAHs from n-alkanes in diesel fuel
- React with OH radicals
- Sample chamber onto PUF
- Extract
- HPLC fractionate
- GC/MS with negative ion  $\text{CH}_4$  chemical ionization for Nitro-PAHs

$$[\text{OH}] = 5 \times 10^6 \text{ radical cm}^{-3}$$

$$\tau_{\text{naphthalene}} = 2.3 \text{ hr}$$

$$\tau_{\text{MN}_s} = 1.2 \text{ hr}$$

$$\tau_{\text{DMN}_s} = 40\text{-}60 \text{ min}$$

# AMBIENT ANALYSES at USC

University of Southern California

Aug. 12-16, 2002

4 time intervals:

07-10:30 hr (direct vehicle emissions)

11-14:30 hr (highest OH radical)

15-18:30 hr (possible start NO<sub>3</sub> chemistry)

19-6:30 hr (overnight, NO<sub>3</sub> radical?)

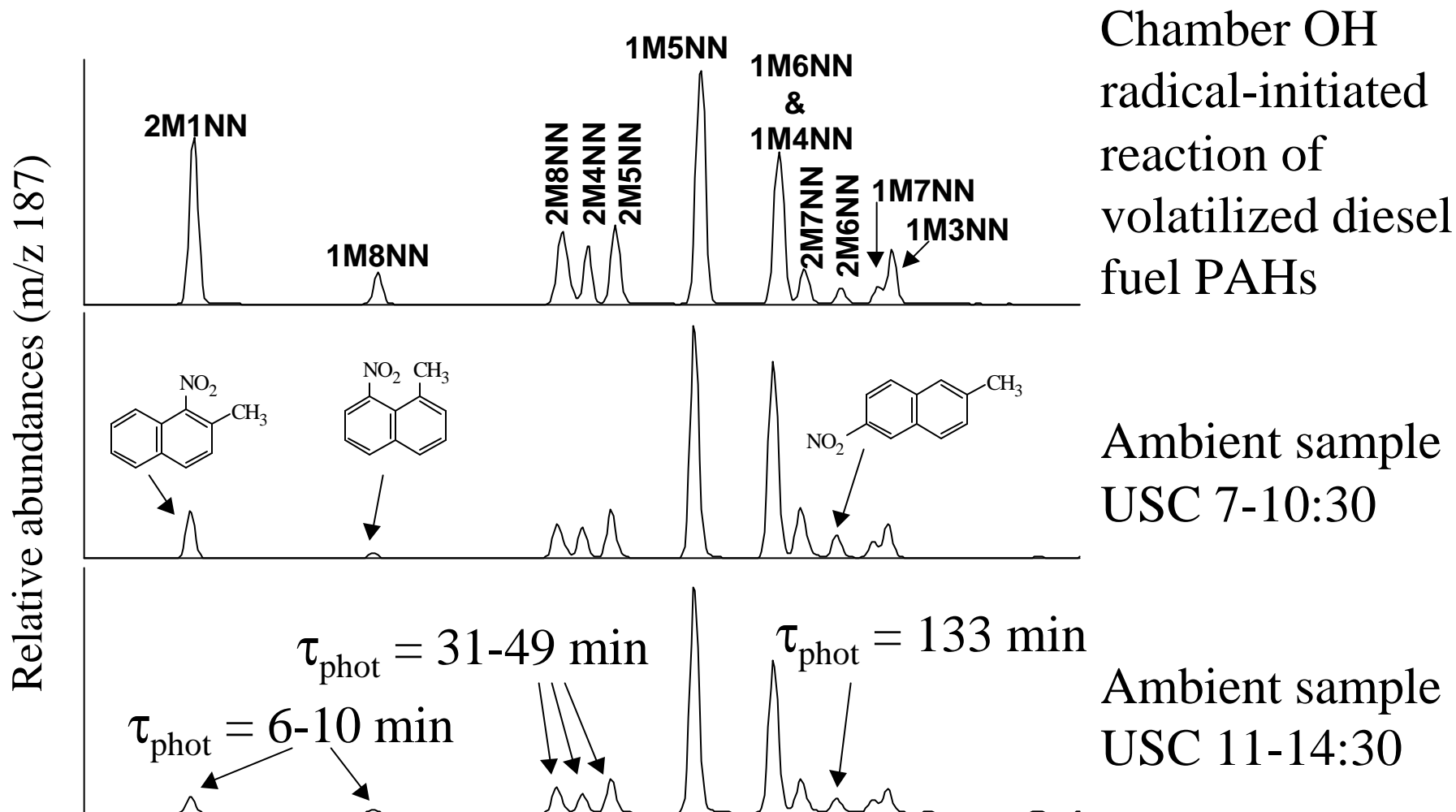
Volatile PAHs on  
Tenax –replicates:

8 samples/day  
analyzed.

Semi-volatile  
nitro-PAHs on  
PUF plugs:

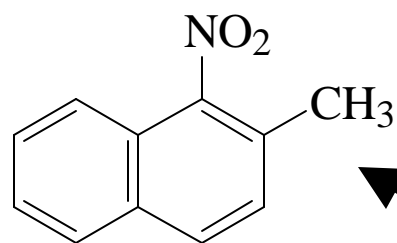
composited to 4  
samples.

# Methylnitronaphthalenes (GC/MS-NCI)

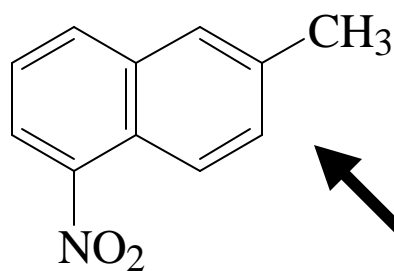




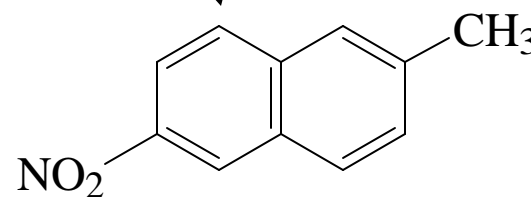
# Calculated Photolysis Lifetimes of Nitro- & Methylnitronaphthalenes



*ortho- & peri-*  
substituted  
elute early



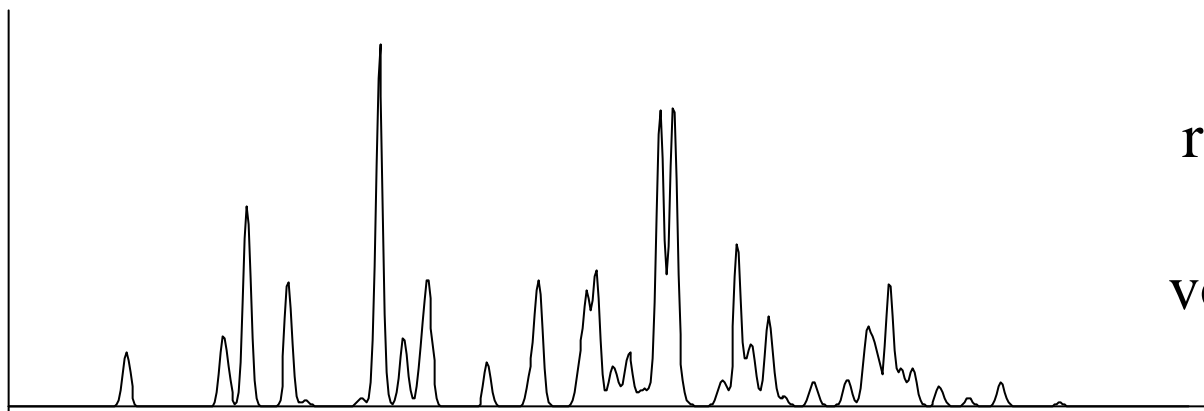
NO <sub>2</sub> on C <sub>1</sub>	$\tau$ (min)	NO <sub>2</sub> on C <sub>2</sub>	$\tau$ (min)
1M8NN	6	1M2NN	31
2M1NN	10	1M3NN	71
1M4NN	22	1M6NN	88
1NN	24	2M6NN	133
2M8NN	31	2NN	177
1M5NN	38		
2M4NN	41		
2M5NN	49		



# Dimethylnitronaphthalenes (GC/MS-NCI)

Chamber OH  
radical-initiated  
reaction of  
volatilized diesel  
fuel PAHs

Relative abundances (m/z 201)



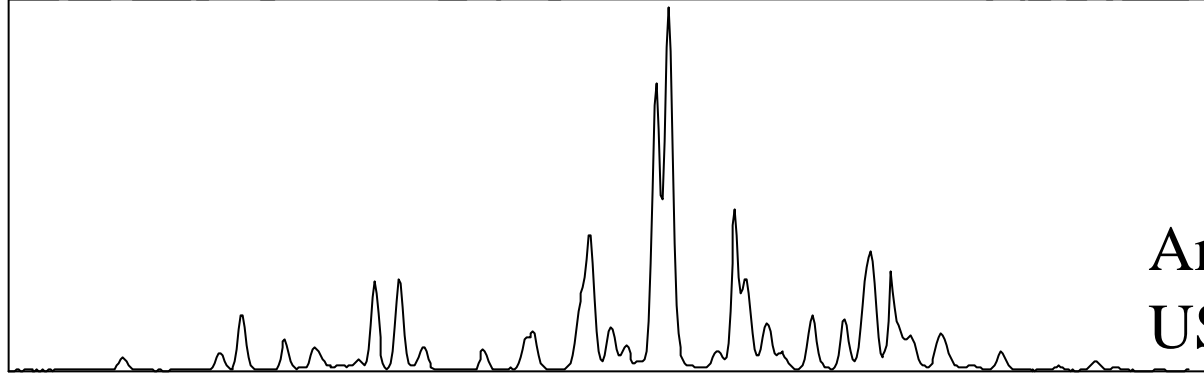
Rapidly Photolyze?



Ambient sample  
USC 7-10:30



Ambient sample  
USC 11-14:30



# Conclusions

- First identification of dimethyl-/ethyl-nitronaphthalenes in ambient air.
- Their presence is attributed mainly to OH radical-initiated reactions of dimethyl-/ethyl-naphthalenes.
- Although the DMNs/ENs concentrations are lower than those of naphthalene and the MNs, the nitrated products are more similar in concentration. In LA during this study:

NNs  $\sim 200\text{-}500 \text{ pg m}^{-3}$

MNNs  $\sim 100\text{-}250 \text{ pg m}^{-3}$

DMNN/ENNs  $\sim 50\text{-}150 \text{ pg m}^{-3}$

# Chemistry of Oxygenated VOCs

(atmospheric reaction products  
of other VOCs)

# Oxygenated VOCs

- Kinetics and Products of OH + 2-methyl-2-pentanol and 4-methyl-2-pentanol.
- Products of OH + 1,2-, 1,3- and 2,3-butanediol and 2-methyl-2,4-pentanediol.
- H-atom abstraction from OH + 2,3-dimethylpentanal, 1,4-cyclohexadiene and 1,3,5-cycloheptatriene.

# Product studies of OH + diols

- 1,2-Butanediol
  - 2,3-Butanediol
  - 1,3-Butanediol
  - 2-Methyl-1,4-pentanediol
- 
- We previously investigated the formation of **selected** products by GC-FID and GC-MS, using collection onto Tenax solid adsorbent.

# Products observed by Tenax/GC

$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$  from  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$

$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_3$  from  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$

$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$  from  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$

$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$  from

$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

- Only hydroxyketone products observed.
- These arise from H-atom abstraction from CH(OH) group(s):



- What about the hydroxyaldehydes such as  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$  formed after H-atom abstraction from the  $\text{CH}_2\text{OH}$  groups?

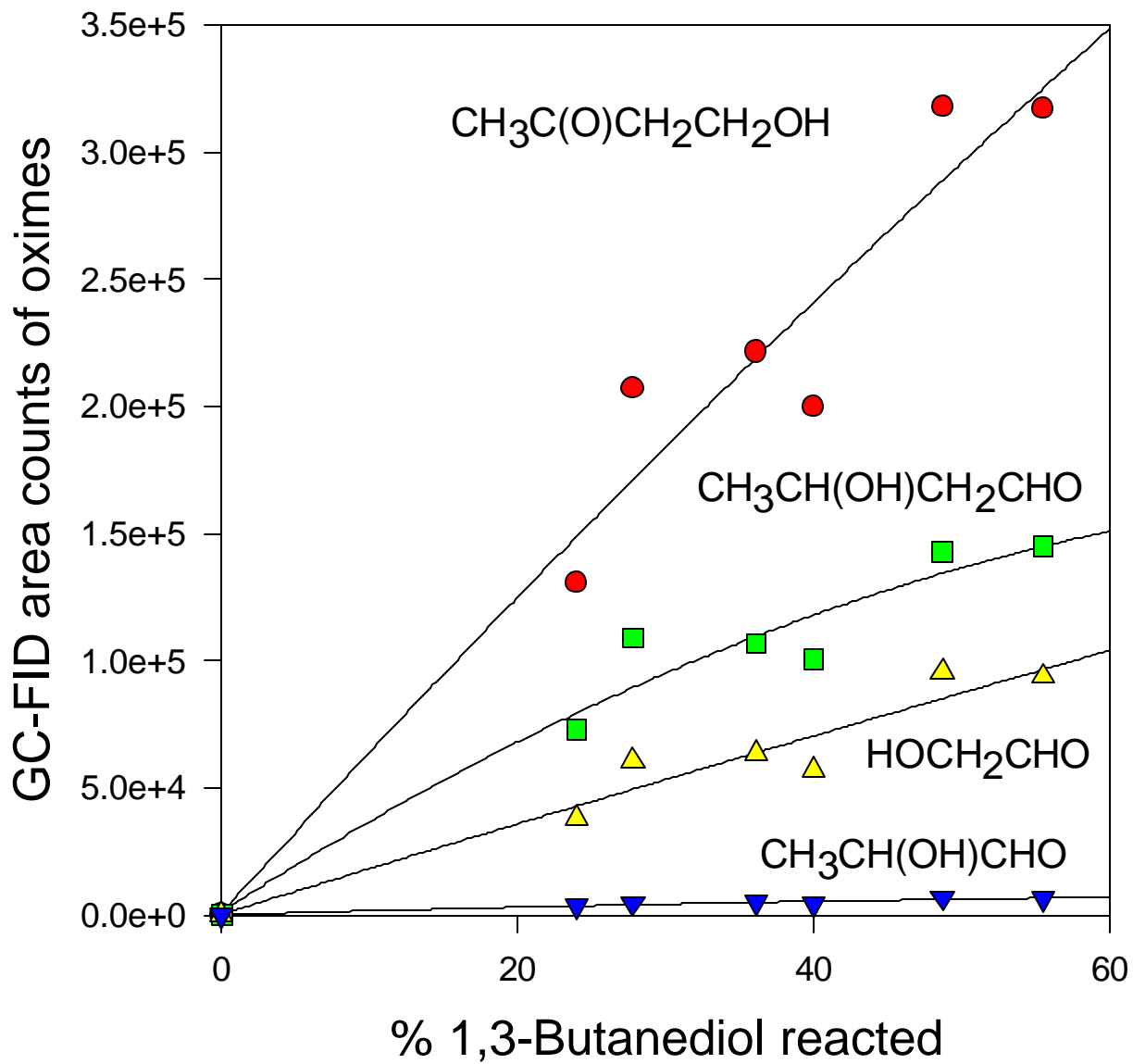


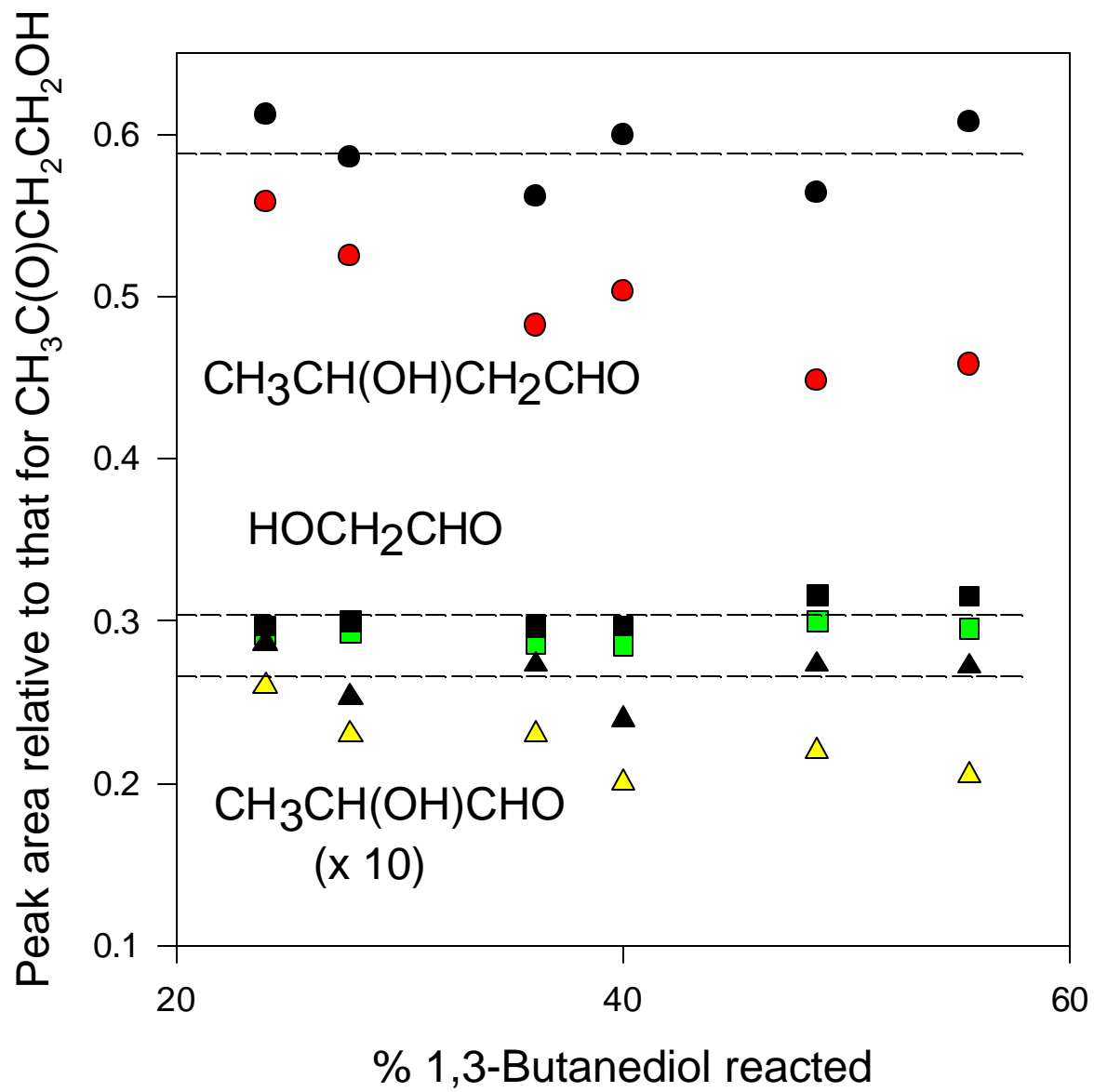
# Hydroxyaldehydes

- Appear not to elute from GC columns unless they are derivatized prior to injection onto the column.
- **Very few are commercially available.**
- API-MS and FT-IR analyses not useful because products are isomeric and because of lack of standards.
- **SPME fibers coated with PFBHA used for collection of hydroxyaldehydes for GC.**

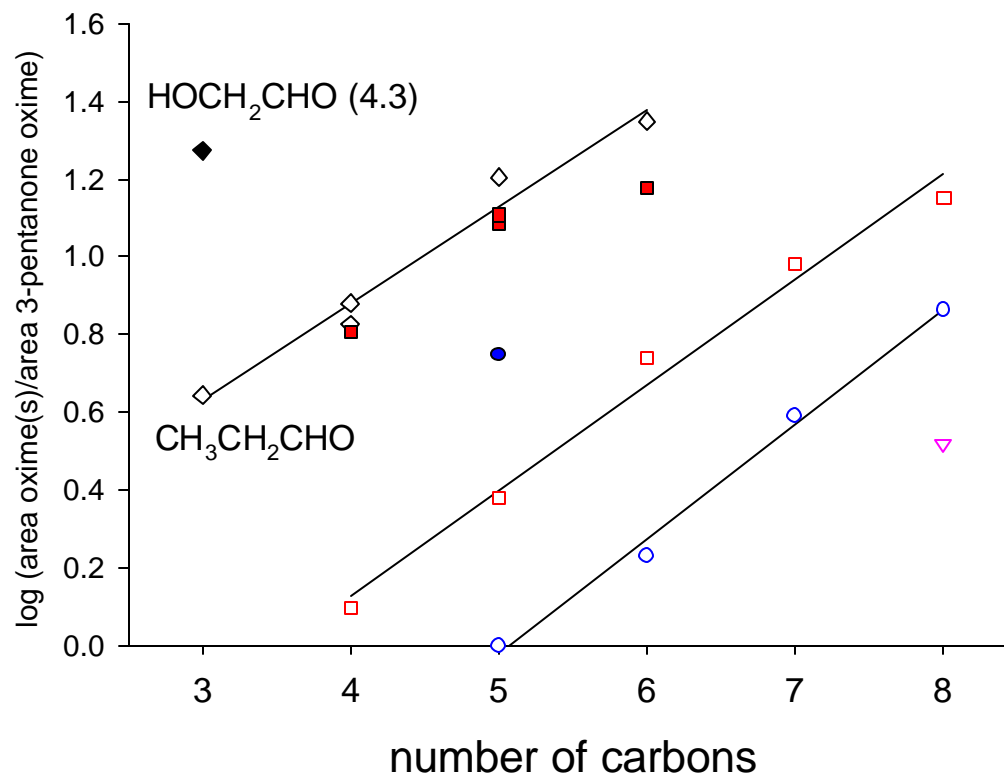
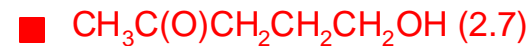
## Products observed by “coated SPME”

diol	product
$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$ $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CHO}$ $\text{HOCH}_2\text{CHO}$
$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$	$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_3$ $\text{CH}_3\text{CH}(\text{OH})\text{CHO}$
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$ $\text{CH}_3\text{CH}(\text{OH})\text{CHO}$ $\text{HOCH}_2\text{CHO}$
$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ $\text{CH}_3\text{CH}(\text{OH})\text{CHO}$





# SPME response increases 5-fold, replacing $-\text{CH}_3$ with $-\text{OH}$



## Products observed by “coated SPME”

diol	product	yield(%)
CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	CH <sub>3</sub> CH <sub>2</sub> C(O)CH <sub>2</sub> OH	66 ± 11
	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CHO	27
	HOCH <sub>2</sub> CHO	10 ± 4
CH <sub>3</sub> CH(OH)CH(OH)CH <sub>3</sub>	CH <sub>3</sub> C(O)CH(OH)CH <sub>3</sub>	89 ± 9
CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>3</sub> CH(OH)CHO	2
	CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>2</sub> OH	50 ± 9
	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CHO	15
	CH <sub>3</sub> CH(OH)CHO	0.7
	HOCH <sub>2</sub> CHO	10 ± 4
(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> CH(OH)CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> C(O)CH <sub>3</sub>	47 ± 9
	CH <sub>3</sub> CH(OH)CHO	24

# OH + 2,3-Dimethylpentanal

- OH + CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH(CH<sub>3</sub>)CHO
- Major reaction pathways is assumed to be H-atom abstraction from the CHO group.
- Determine the importance of H-atom abstraction from 2-position C-H bond.

- Analysis of products by GC-FID and *in situ* FT-IR spectroscopy.
- 3-Methyl-2-butanone,  $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)_2$ , arises only from H-atom abstraction at the 2-position C-H bond.
- Yield of 3-methyl-2-butanone =  $5.4 \pm 1.0\%$ .
- H-atom abstraction from the 3-position C-H bond expected to be more important (27%), but unique product(s) not formed.



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