

# ATMOSPHERIC CHEMISTRY OF ALKANES – RECENT DEVELOPMENTS

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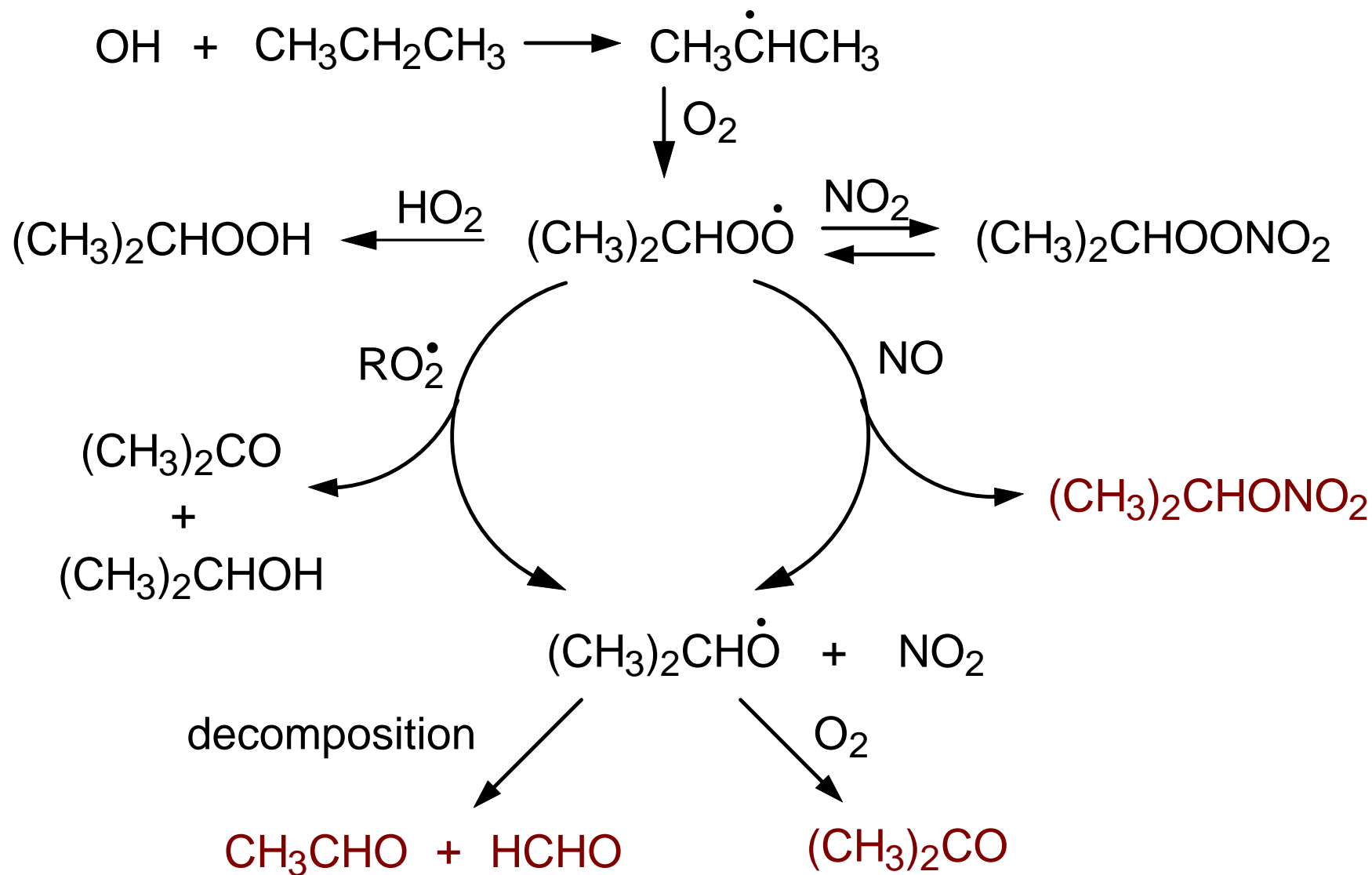
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# Alkanes

- 50-60% of reformulated gasolines and of VOCs in vehicle exhaust.
- ~50% of non-methane VOCs in air in urban areas.
- React with OH radicals (dominant) and NO<sub>3</sub> radicals (generally minor) in the troposphere.
- Lifetimes of C<sub>3</sub>-C<sub>10</sub> alkanes range from ~1 day (*n*-decane) to ~10 days (propane, neopentane).

# OH + propane in the atmosphere

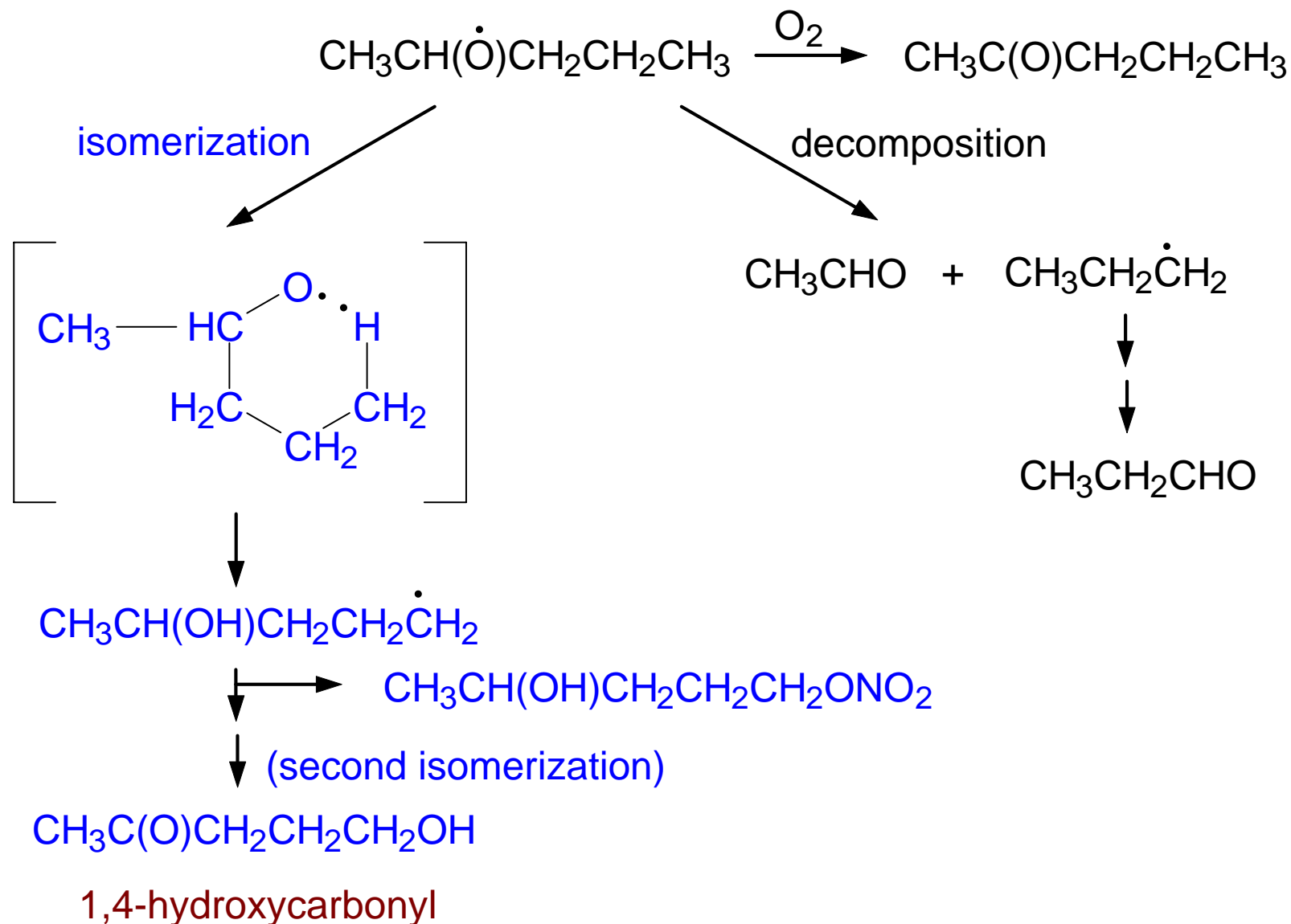


# Product yields (as of 1982-1994)

alkane	% carbonyls	% nitrates	% missing
<i>n</i> -butane	84	8	8
<i>n</i> -pentane	~30	12	~58
<i>n</i> -hexane	“low”	21	high

From data in Carter *et al.*, 1976; Atkinson *et al.*, 1982.

Missing products postulated to be 1,4-hydroxycarbonyls, formed after alkoxy radical isomerization (Carter *et al.*, 1976)



# Progress 1995-2001

- Eberhard *et al.* (1995) identified 5-hydroxy-2-hexanone as a product of OH + *n*-hexane and from 2-hexyl nitrite photolysis by HPLC after derivatization.
- We observed hydroxycarbonyls from OH + C<sub>4</sub>-C<sub>8</sub> *n*-alkanes using API-MS analyses in positive ion mode (Atkinson *et al.*, 1995; Kwok *et al.*, 1996) and in negative ion mode as NO<sub>2</sub><sup>-</sup> adducts (Arey *et al.*, 2001).

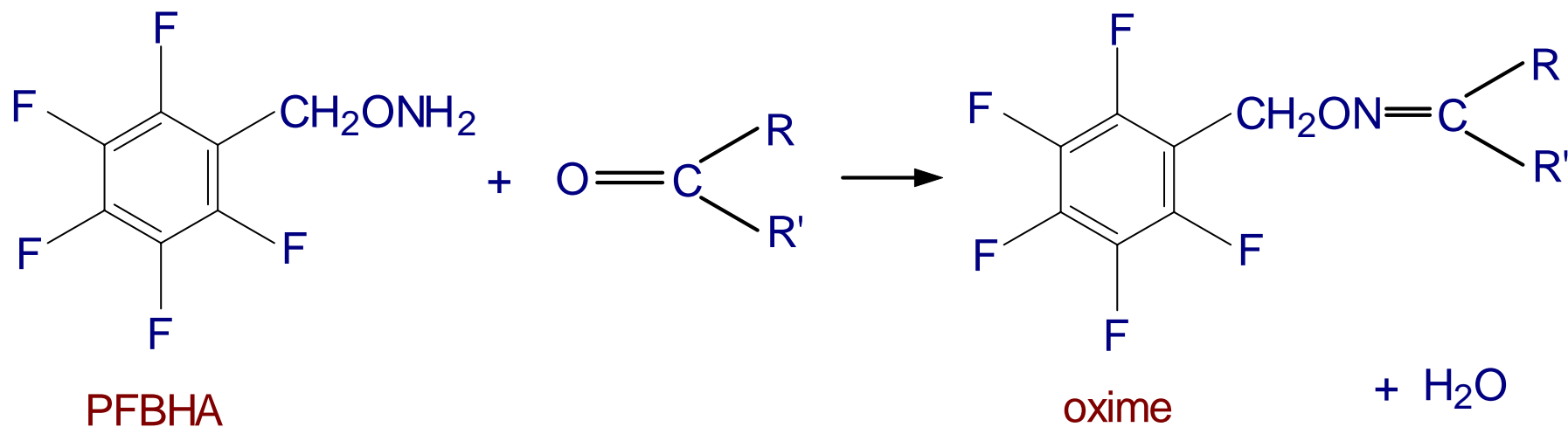
## Product yields (%) in air at 5% RH

alkane	carbonyls	nitrates	hydroxy-carbonyls	hydroxy-nitrates
<i>n</i> -pentane	50	10.5	36	2.6
<i>n</i> -hexane	10	14	53	4.6
<i>n</i> -heptane	<1	18	46	4.7
<i>n</i> -octane	<1	23	27	5.4

Carbonyl data from 1995-96 studies

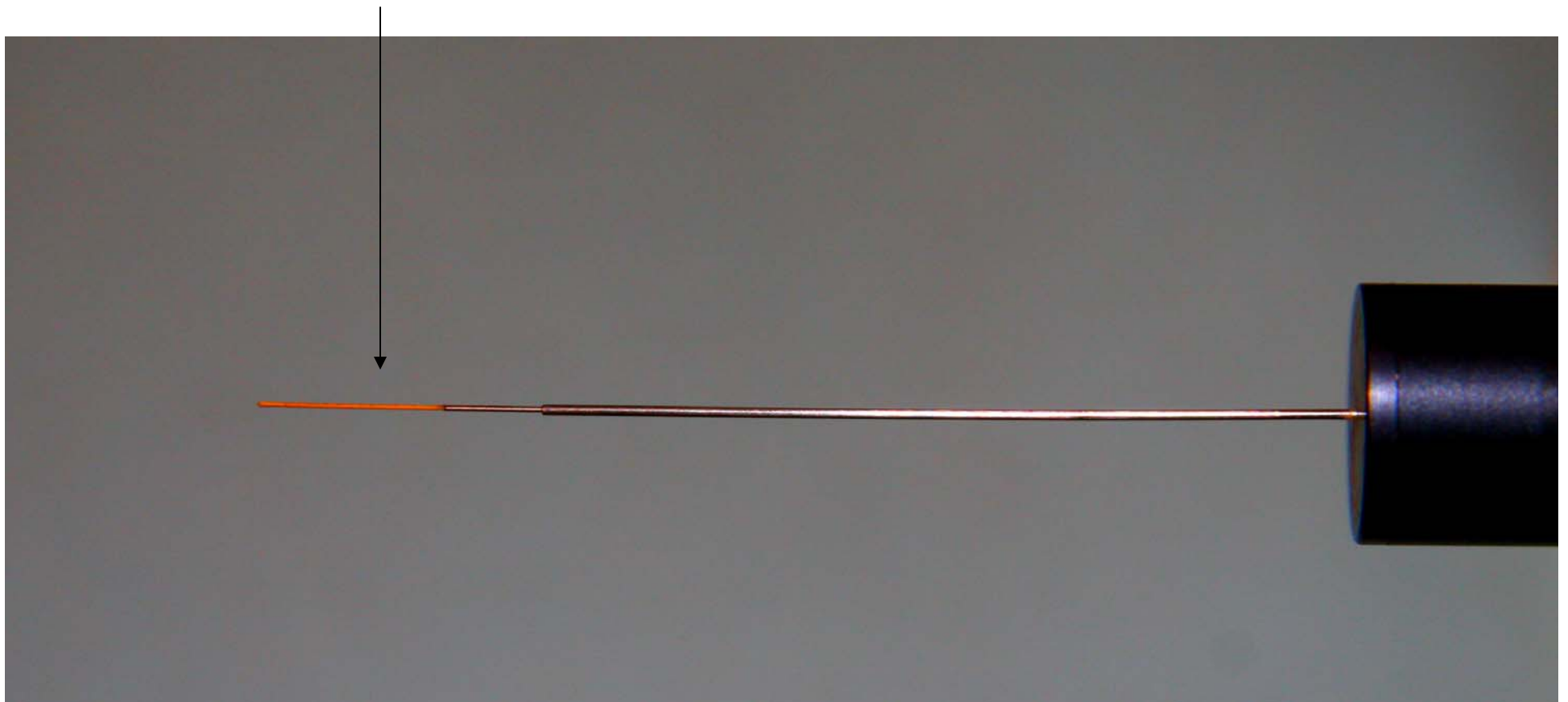
# Solid-Phase MicroExtraction fibers

Can be coated with a chemical for on-fiber derivatization of carbonyl-containing compounds.



Fibers are retractable. After coating with PFBHA, the fibers are exposed to the chamber contents with the chamber mixing fan on for typically 5 min.

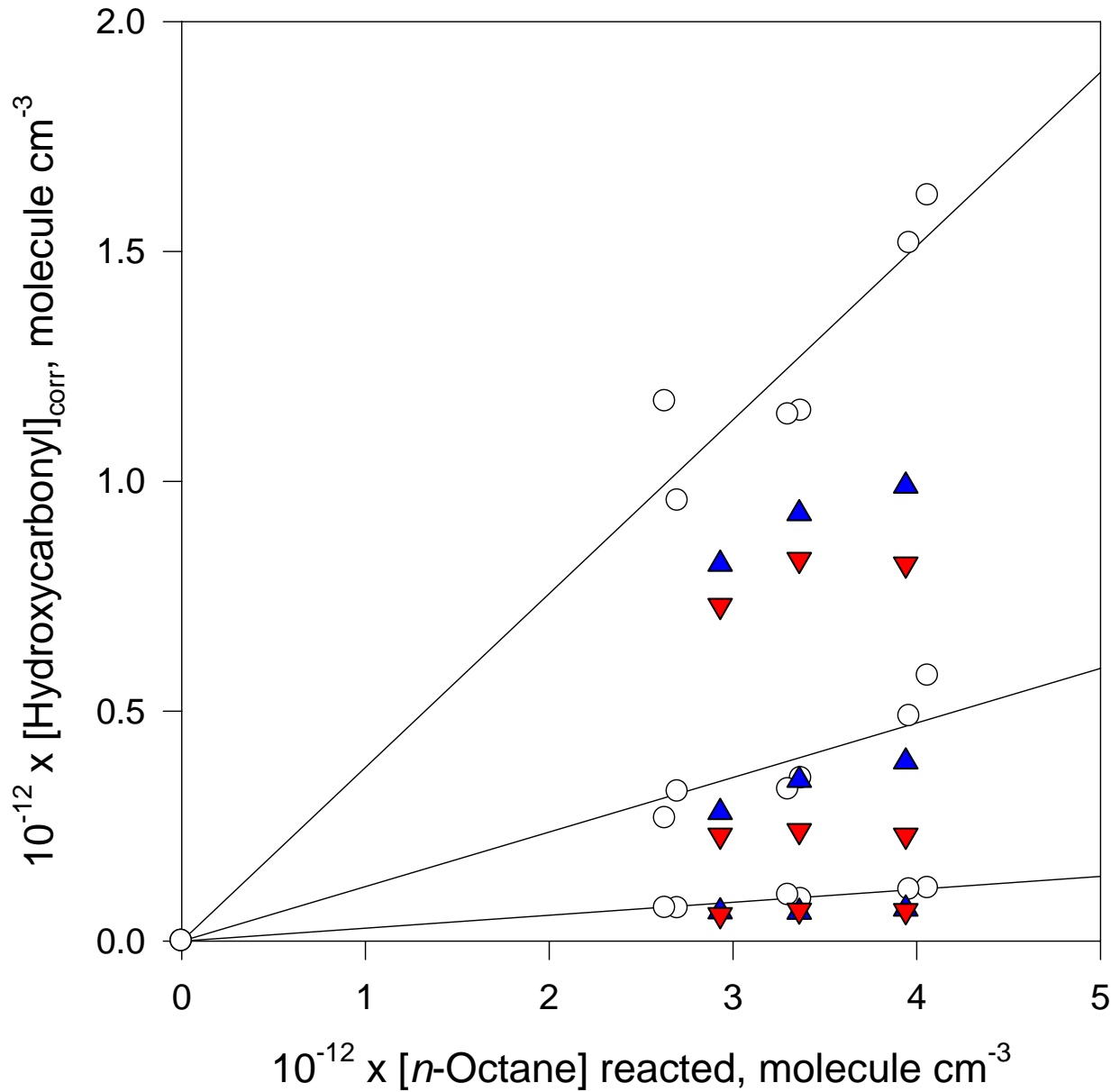
Fiber, ~20 mm long



The mass spectra from GC-MS analyses of the OH radical-initiated reactions of C<sub>5</sub>-C<sub>8</sub> *n*-alkanes allowed 1,4-hydroxycarbonyls to be identified. In the presence of NO, all possible 1,4-hydroxycarbonyls are formed:

- 2 from *n*-pentane (5-hydroxy-2-pentanone is commercially available).
- 3 from *n*-hexane.
- 4 from *n*-heptane.
- 5 from *n*-octane.

# OH + *n*-octane



6-hydroxy-3- + 5-  
hydroxy-2-octanone

Open: 50% RH

Blue: 5% RH 1<sup>st</sup>

Red, 5% RH, 2<sup>nd</sup>

7-hydroxy-4-octanone

4-hydroxyoctanal

## Product yields (%) in air at 50% RH

alkane	carbonyls	nitrates	hydroxy-carbonyls	hydroxy-nitrates
<i>n</i> -pentane	50	10.5	54 (36)	2.6
<i>n</i> -hexane	10	14	57 (53)	4.6
<i>n</i> -heptane	<1	18	51 (46)	4.7
<i>n</i> -octane	<1	23	53 (27)	5.4

Yields in parentheses from API-MS in air at 3-5% RH

# OH + alkane products

- For  $\geq C_5$  *n*-alkanes at room temperature, if alkoxy radical isomerization can occur it dominates, leading in the presence of NO to 1,4-hydroxynitrates and 1,4-hydroxycarbonyls.
- For larger *n*-alkanes, products are then alkyl nitrates, 1,4-hydroxynitrates and 1,4-hydroxycarbonyls.

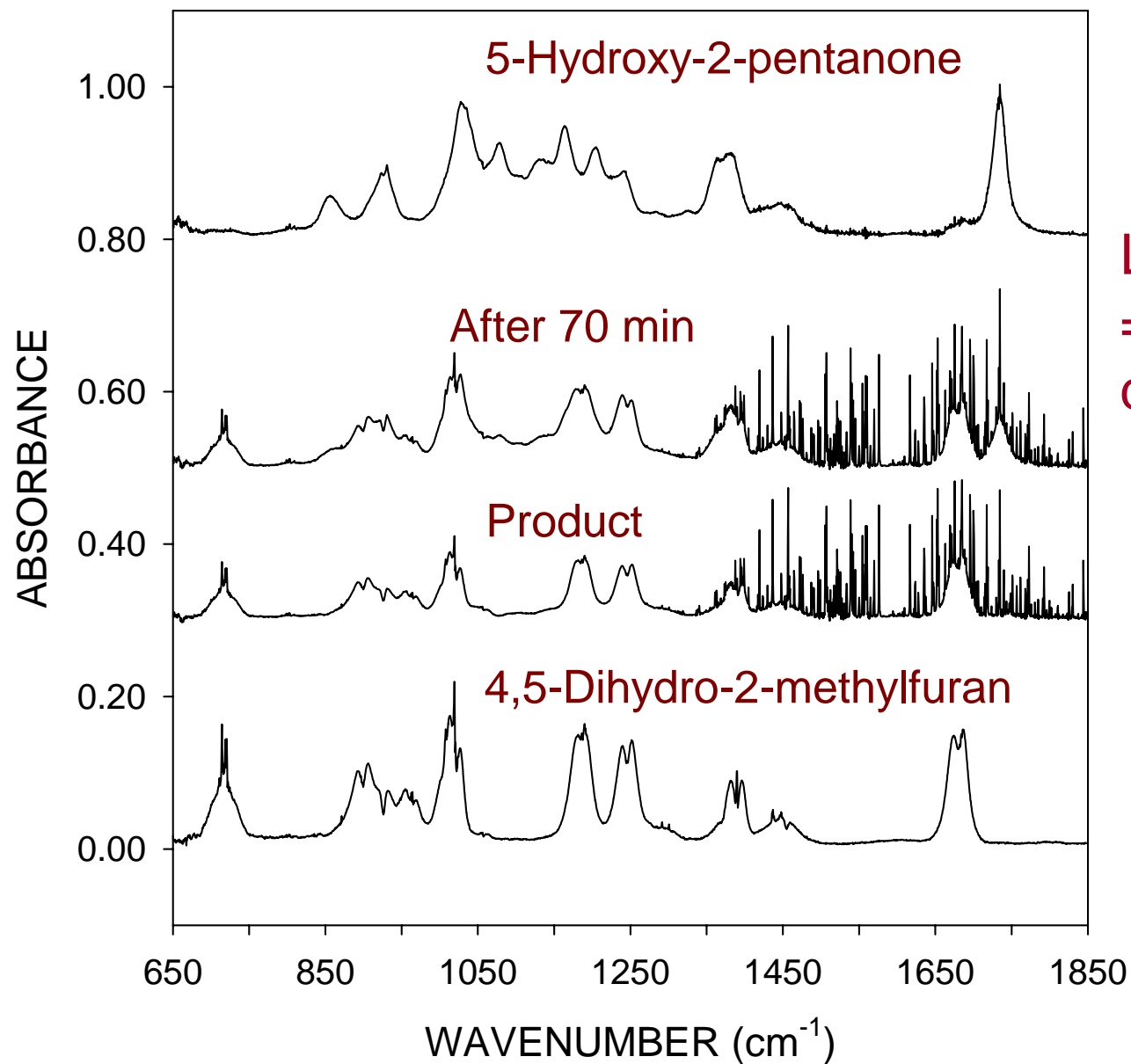
Effect of branching on product distribution:  
(TMP, trimethylpentane; DEH, diethylhexane)

alkane	from O <sub>2</sub> reaction	from decomp.	from isomer.
<i>n</i> -octane	<1%	<1%	~75%
2,2,4-TMP		~40%	≥11%
2,3,4-TMP		50-55%	25-30%
2,3-DEH		~73%	~16%

# Atmospheric behavior of 1,4- hydroxycarbonyls: 5-hydroxy-2-pentanone

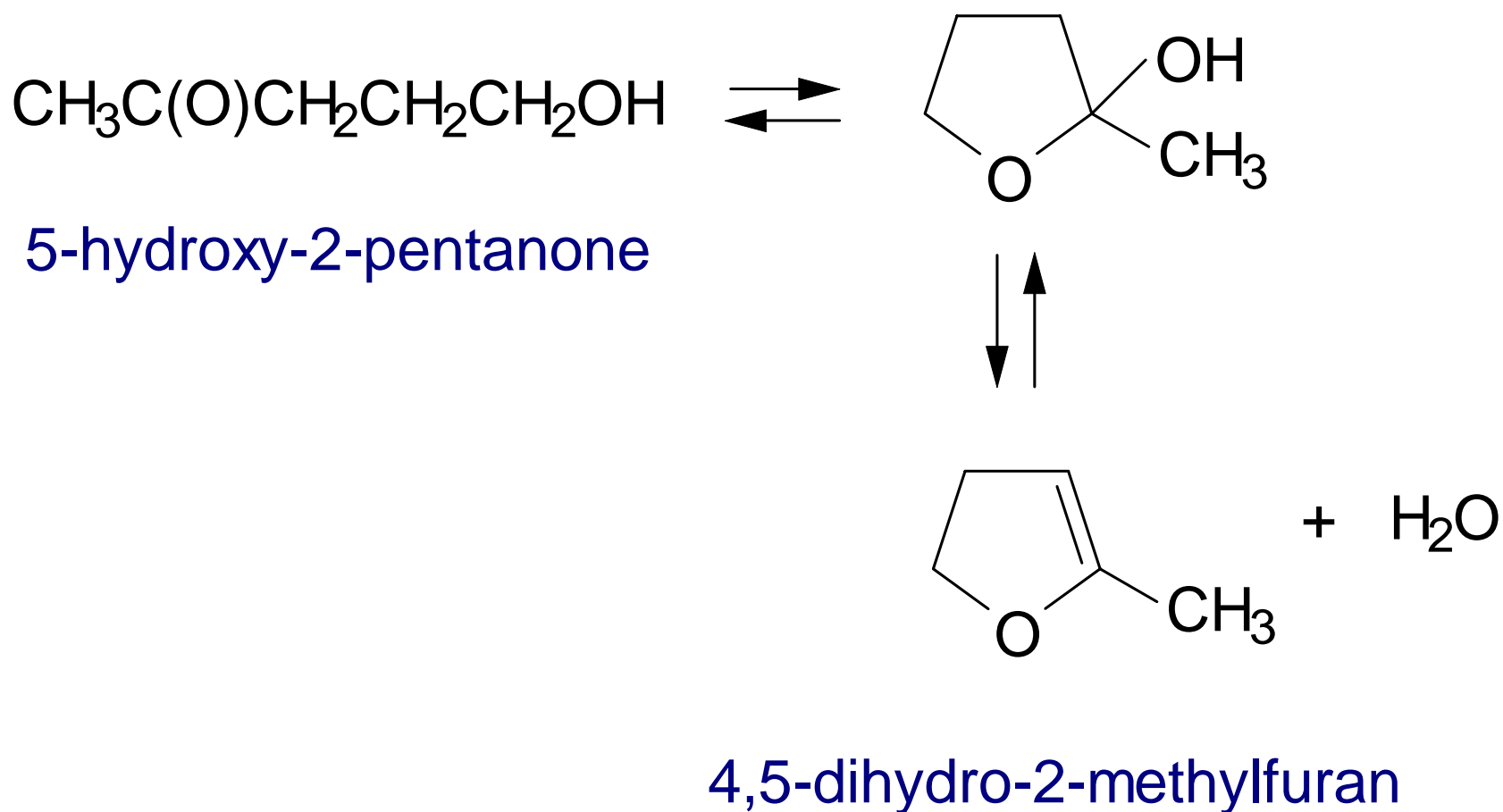
- This is the only 1,4-hydroxycarbonyl commercially available.
- Can be monitored by FT-IR spectroscopy and its atmospheric chemistry studied (so we thought!).

# FT-IR spectra of a 5-hydroxy-2-pentanone – N<sub>2</sub> mixture



Lifetime of 5H<sub>2</sub>PO  
= 1.1 hr at 298 K in  
dry air.

4,5-Dihydro-2-methylfuran is stable in dry air but converts back to 5H2PO at 5% relative humidity, with a lifetime of 3.5 hr.



## Reactions of 5-hydroxy-2-pentanone (5H2PO) and 4,5-dihydro-2-methylfuran (45DH2MF)

- Reactions of 4,5-dihydro-2-methylfuran with OH and NO<sub>3</sub> radicals and O<sub>3</sub> studied in dry air using FT-IR.
- Used coated-SPME fibers to study the OH radical reaction with 5-hydroxy-2-pentanone at ~5% RH.

4,5-Dihydro-2-methylfuran reacts very rapidly with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub>, with room temperature rate constants (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) of:

	OH	NO <sub>3</sub>	O <sub>3</sub>
5H2PO	1.6 x 10 <sup>-11</sup>		
45DH2MF	2.2 x 10 <sup>-10</sup>	1.7 x 10 <sup>-10</sup>	3.5 x 10 <sup>-15</sup>

Daytime lifetimes are then:

*n*-pentane, 1.5 days (OH)

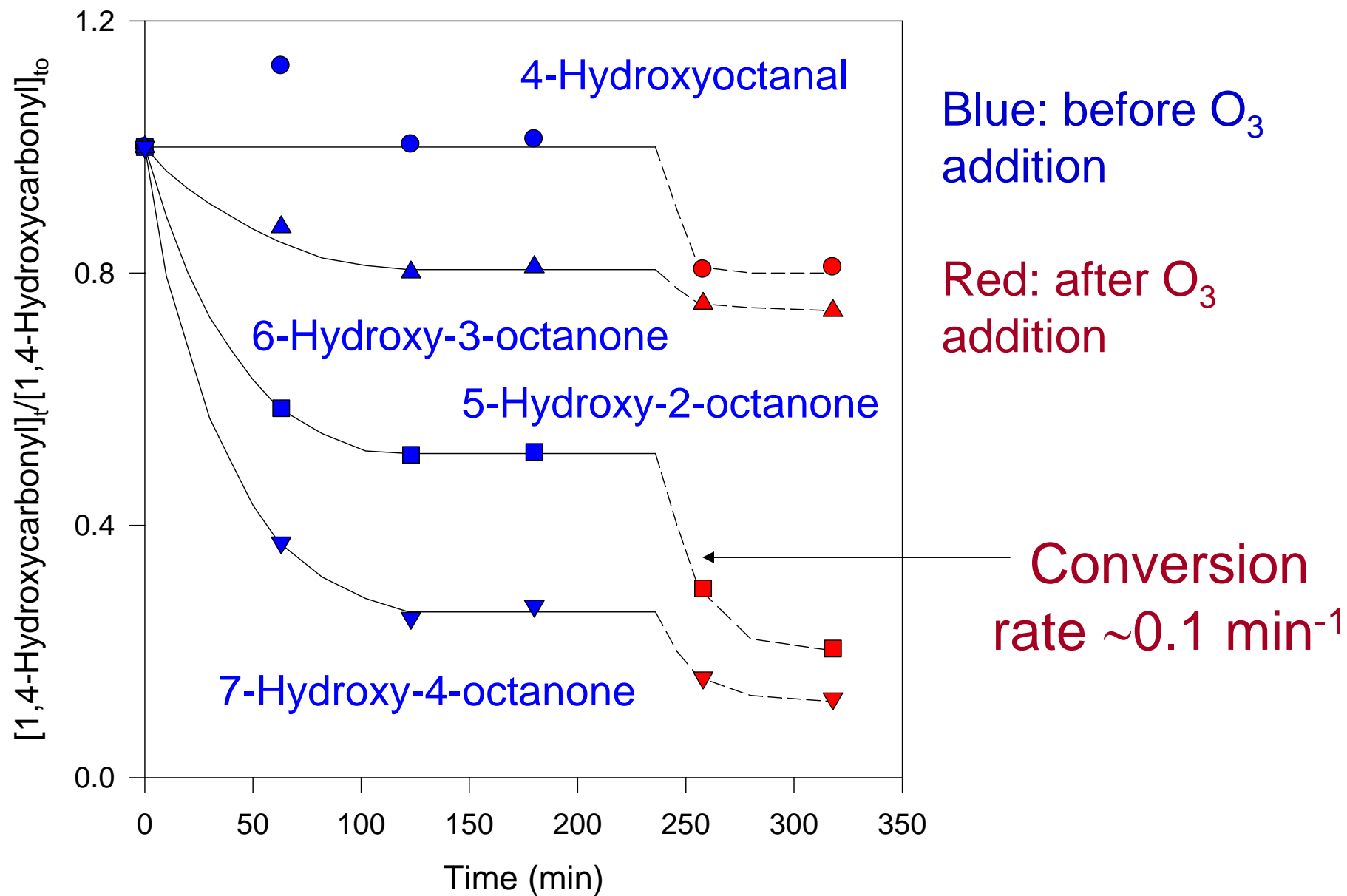
5-hydroxy-2-pentanone, 9 hr (OH)

4,5-dihydro-2-methylfuran, 38 min (OH), 7 min (O<sub>3</sub>)

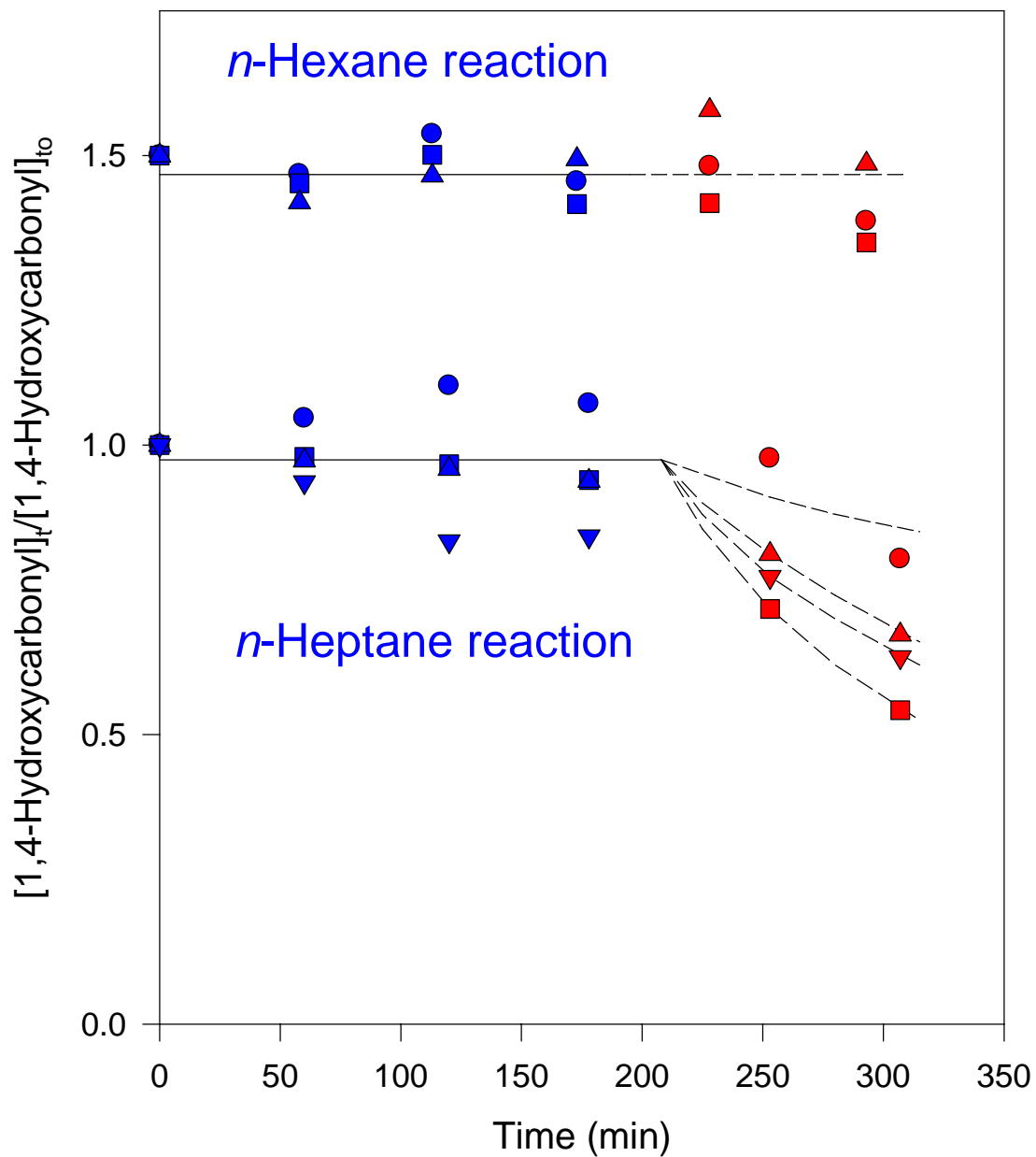
# Behavior of 1,4-hydroxycarbonyls as a function of water vapor concentration

- Generate the 1,4-hydroxycarbonyls *in situ* from OH + *n*-alkane.
- Monitor the 1,4-hydroxycarbonyl concentrations by coated-SPME/GC-FID.
- Add O<sub>3</sub> later in the experiment to remove (by reaction) any dihydrofurans present.

OH + *n*-octane, 5% RH, [H<sub>2</sub>O] = 3 × 10<sup>16</sup> molecule cm<sup>-3</sup>



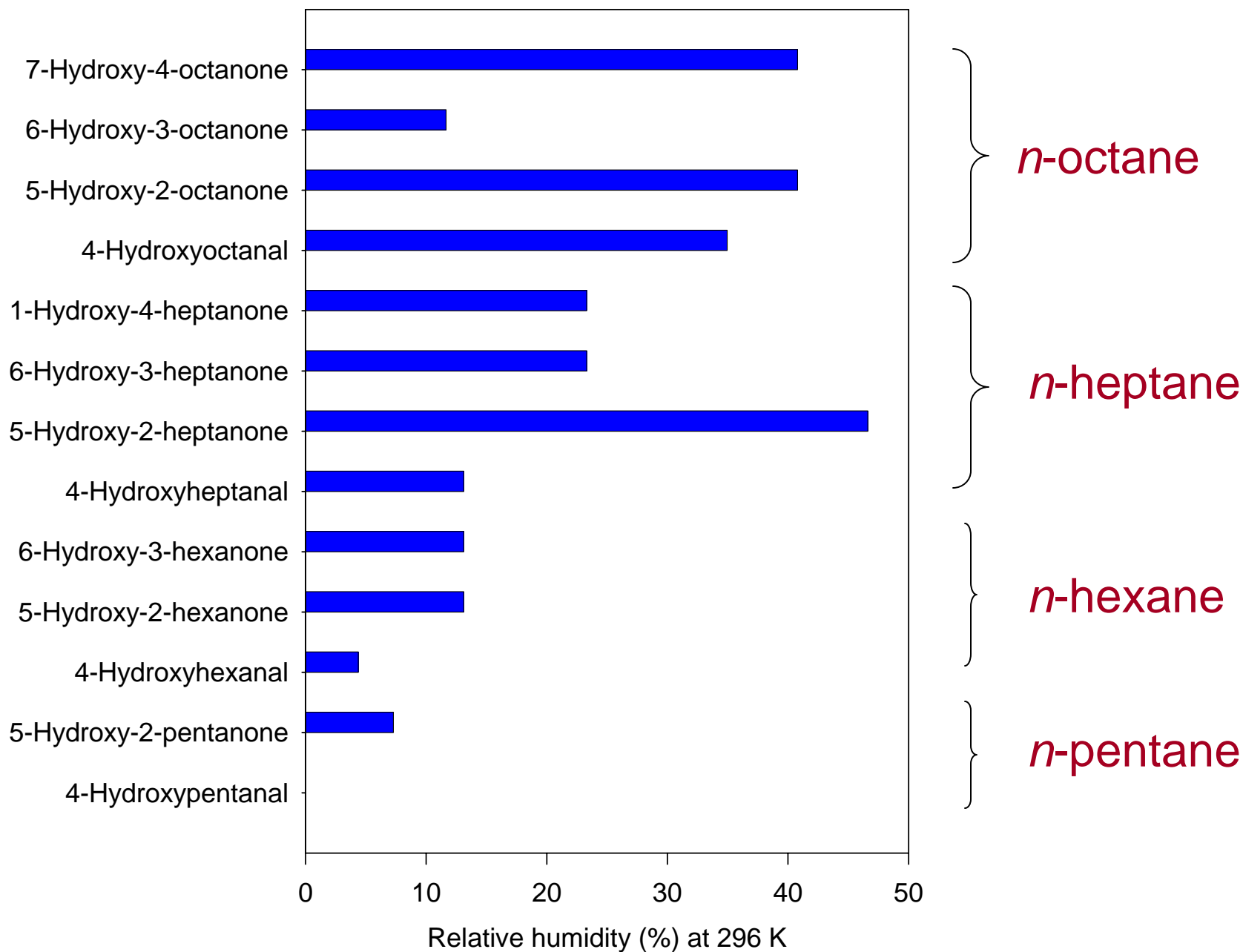
# OH + *n*-hexane (27% RH) and *n*-heptane (15% RH)



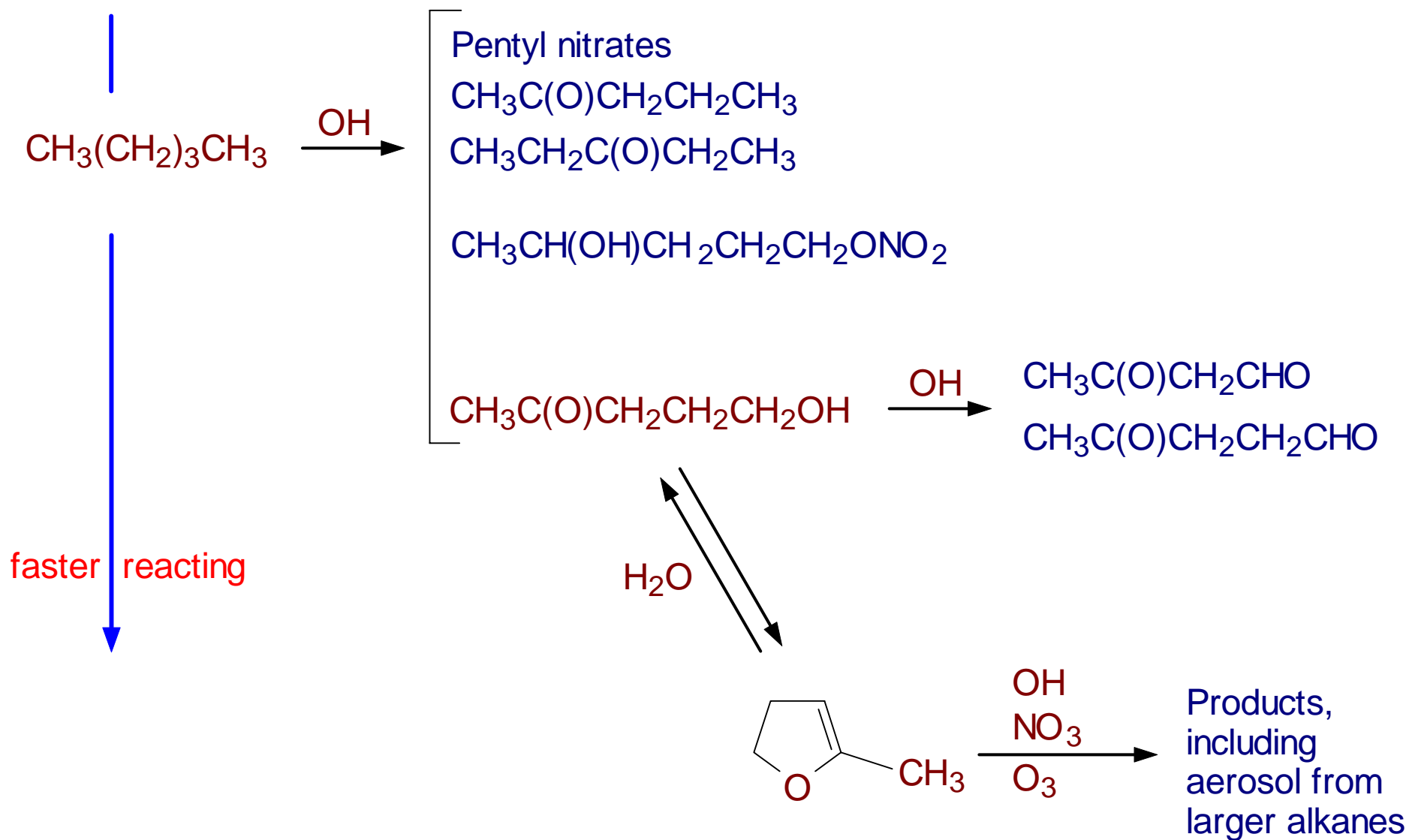
Blue: before  $O_3$   
addition

Red: after  $O_3$   
addition

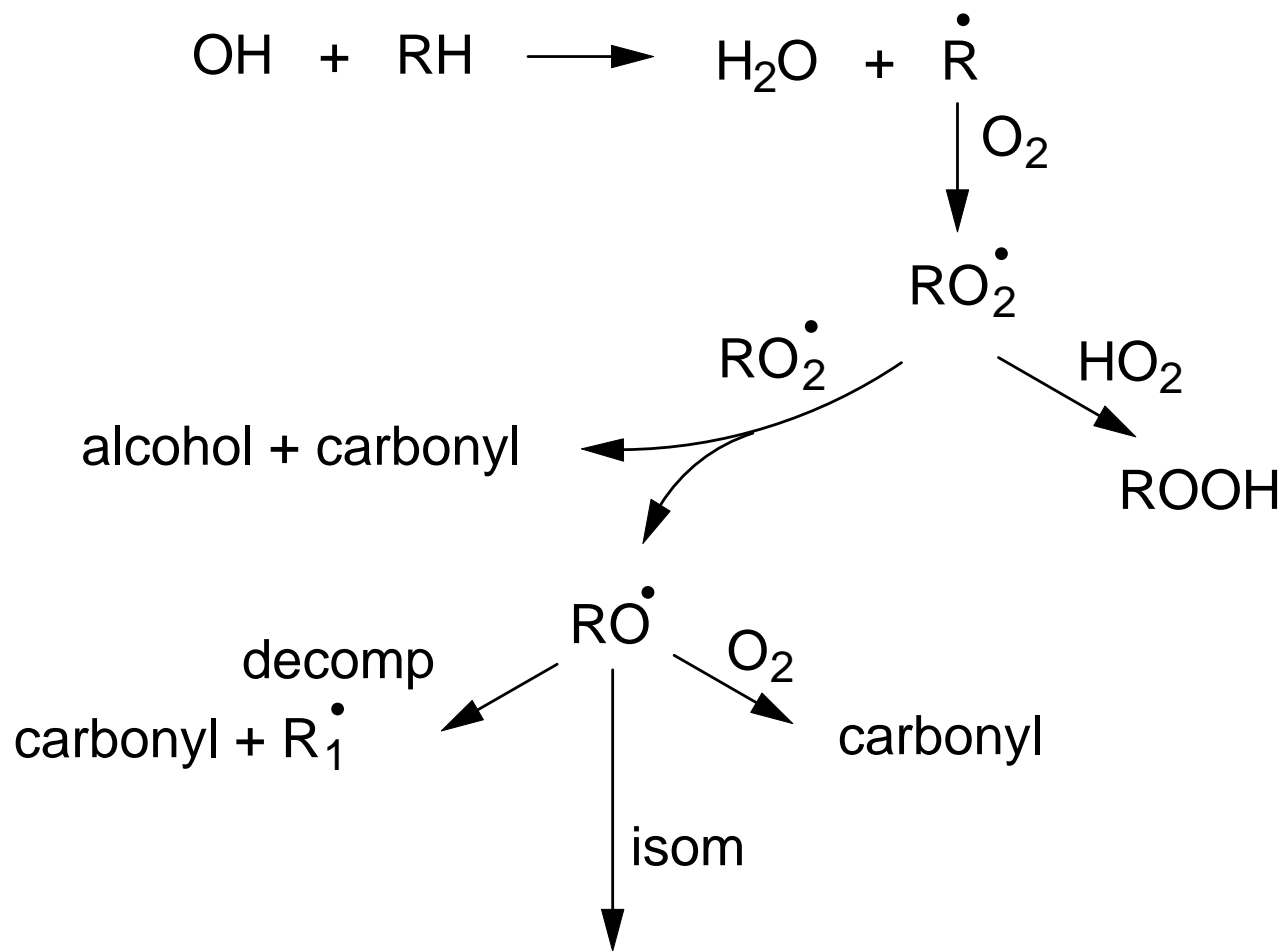
# Relative humidities where dihydrofuran formation is important



In summary, for *n*-pentane in the presence of NO:



# OH + alkanes in the absence of $\text{NO}_x$



1,4-hydroxycarbonyl

1,4-diol

1,4-hydroxyhydroperoxide

- Generate OH radicals from  $O_3$  + alkene.
- Observe the same 1,4-hydroxycarbonyls as in the presence of NO, but in ~10-fold lower yields (as expected).
- Observe pentanones and pentanols from *n*-pentane in 30% yield (39% from Cl atom-initiated reaction).
- Also observe 1,4-dicarbonyls such as  $CH_3C(O)CH_2CH_2CHO$  (~5% yield) from *n*-pentane. It is not obvious how these are formed, unless from dehydration of  $CH_3C(O)CH_2CH_2CH_2OOH$  which then implies isomerization of  $CH_3CH(OH)CH_2CH_2CH_2OO\bullet$  radicals.

# SOA from OH + alkanes

Paul Ziemann and his group conclude:

- SOA formation due, at least in part, to formation of dihydrofurans and their further reaction with OH radicals to form substituted tetrahydrofurans.
- SOA yields in absence of  $\text{NO}_x$  are lower than in presence of  $\text{NO}_x$ , consistent with lower formation yields of 1,4-hydroxycarbonyls (and therefore of dihydrofurans) in the absence of  $\text{NO}_x$ .

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