Dependence of Alkyl Nitrate Yields on Structure for Mid-Sized Alkanes

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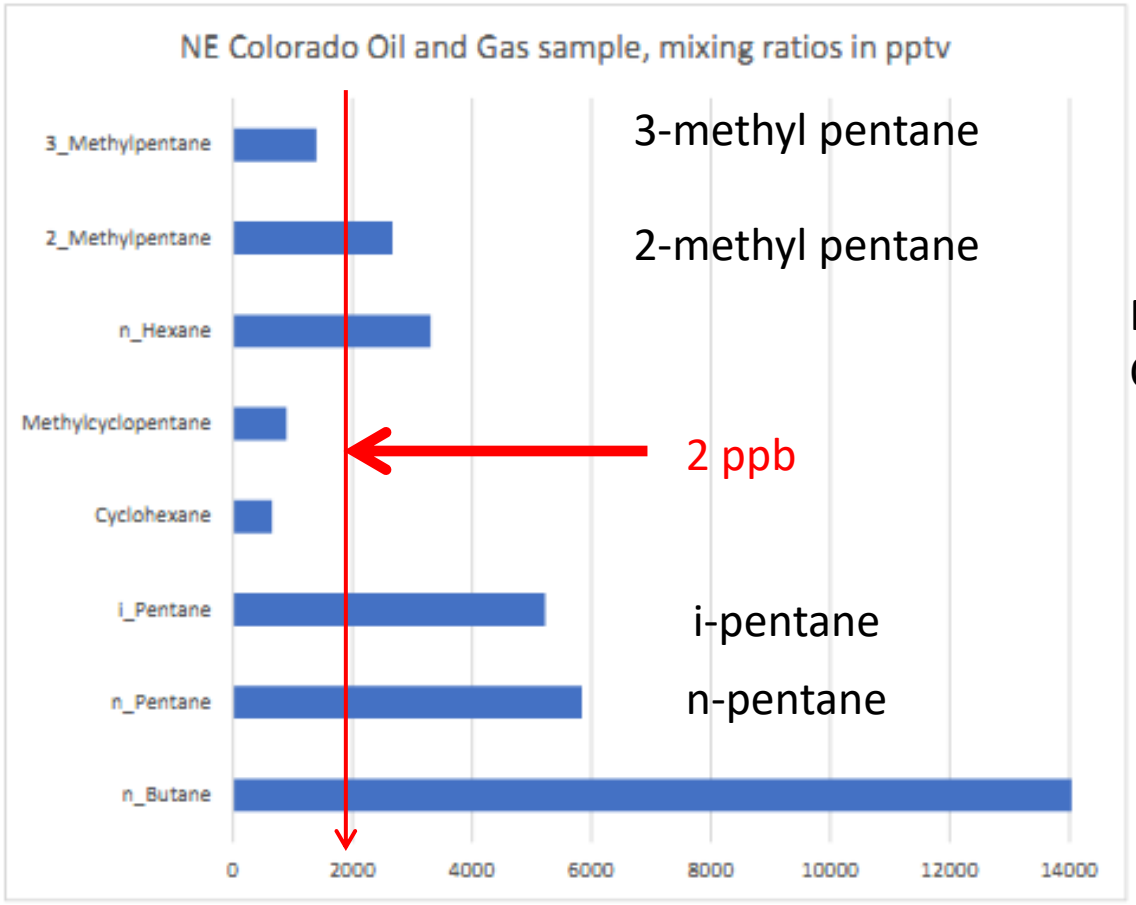
Importance of Alkyl Nitrates?

- Alkyl nitrates are formed from alkanes in atmosphere.
  - $OH + RH (+ O_2) \rightarrow RO_2$
  - $RO_2 + NO \rightarrow RO + NO_2$ Major channel
  - $RO_2 + NO \rightarrow RONO_2$ Minor channel (α 0-30%)
  - $NO_2 + h\nu (+ O_2) \rightarrow NO + O_3$ Ozone formation

- Hence, the formation of alkyl nitrates reduces ozone formation (less available NOx)
- Alkyl nitrates can be used as a measure of ozone formation
- Lifetimes in atmosphere days to weeks
- *Analogous channel following addition of OH to alkenes*

Composition of C_4-C_6 Alkanes in NE Colorado



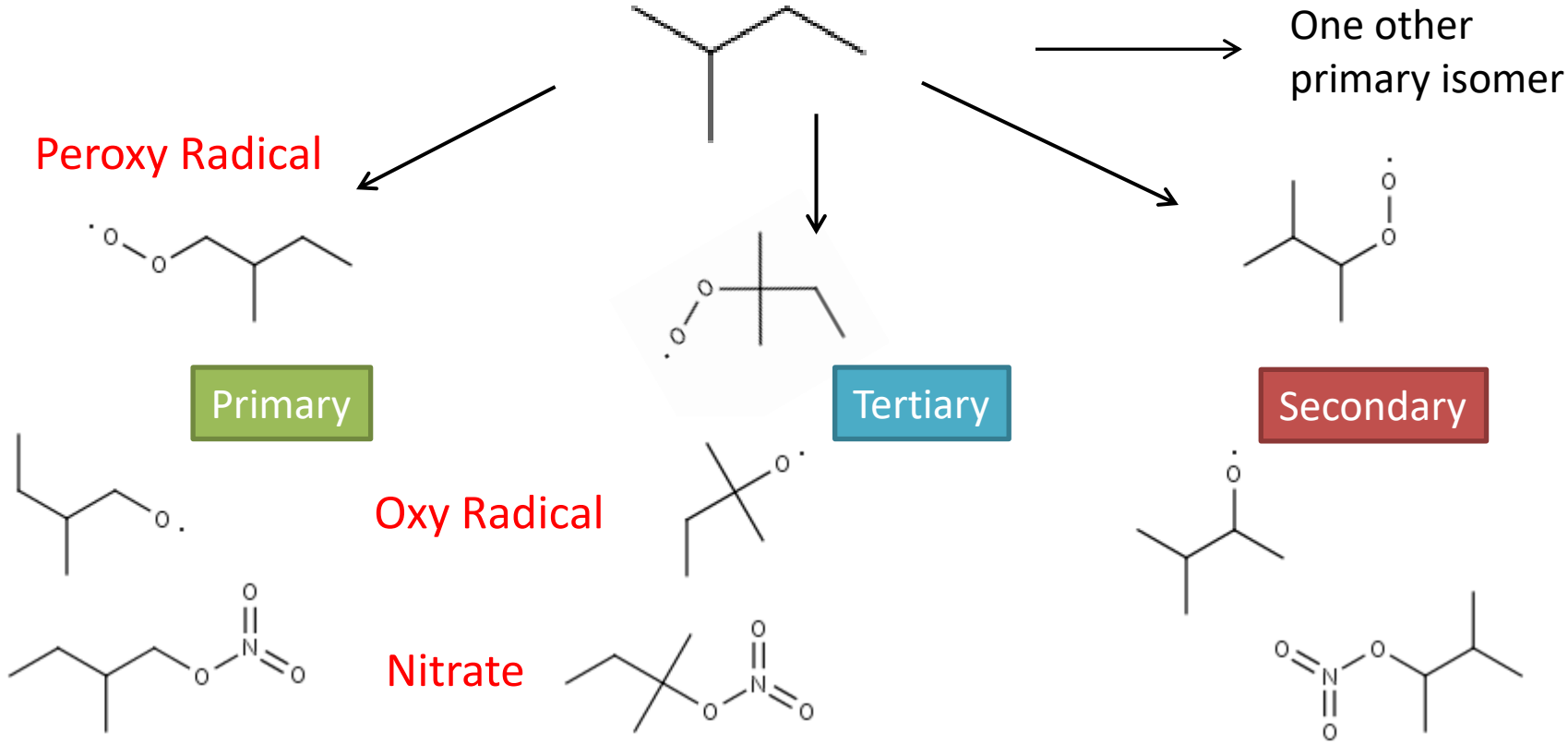
Flight altitude 300 m
Concentrations often > 1 ppb

Whole Air Samples taken and analyzed by D. Blake et al. at U.Cal. Irivine
Many branched alkanes – Rich data set for analysis

One Example on Nomenclature

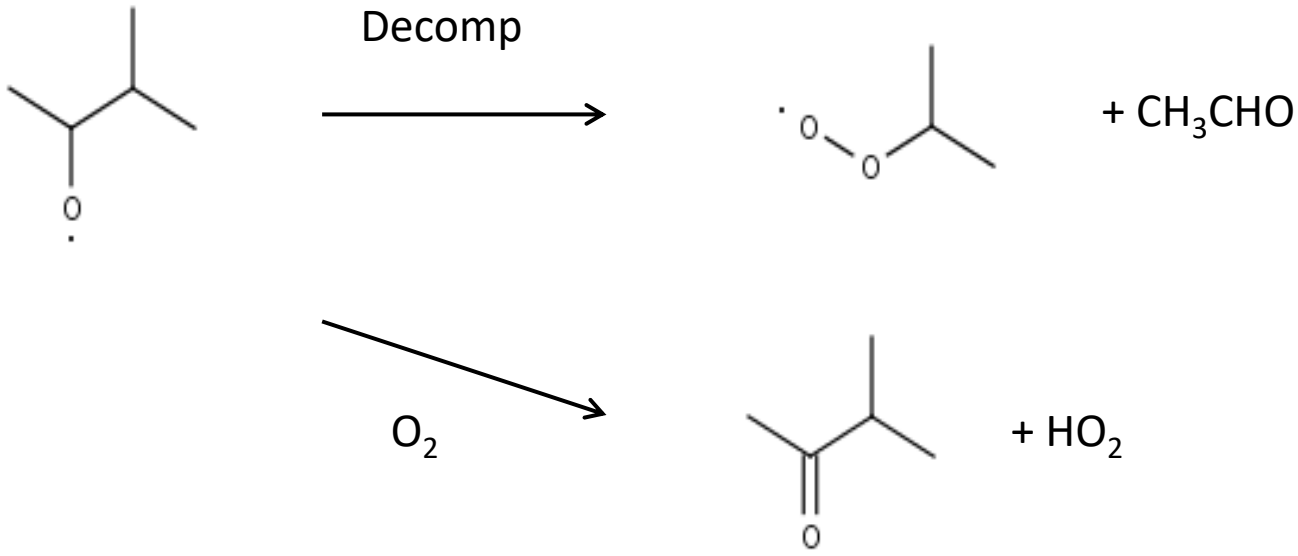
Isopentane (2-methyl butane)

$(CH_3)_2CHCH_2CH_3$



Reactions of subsequent radicals

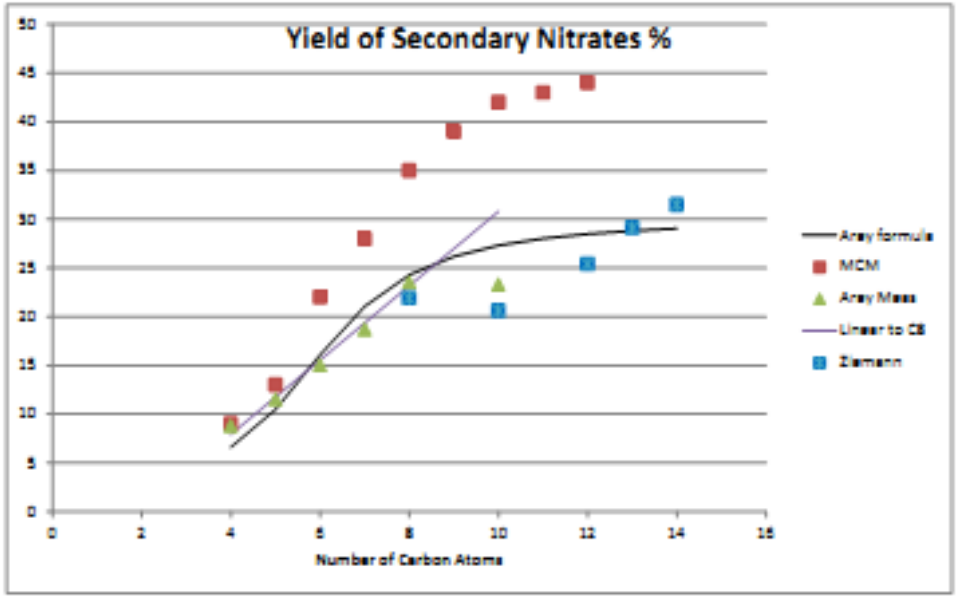
- The reactions of the alkoxy radicals determine the other products.
- We can use products to get mechanistic information (carbonyls, smaller nitrates, PAN)



What do we know?

- Most work done in 1980s by Atkinson et al. (basis for models)
  - linear and branched alkanes
  - Pressure and T-dep
  - Parameterization (squares)→ for secondary nitrates

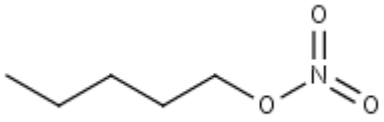
  Yields leveled out at ~45%



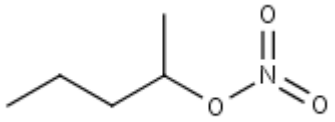
- Yield of tertiary and primary nitrates roughly 0.4x secondary
- Yields revised in 2001 by Arey et al. for secondary $RONO_2$
- Maximum yield reduced to ~30% (better calibrations)

Are primary and tertiary yields higher?

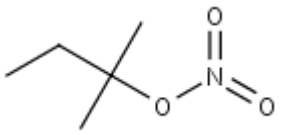
- Field measurements (Flocke et al. 1998):
  - Tertiary nitrate from isopentane not consistent with Atkinson
- Espada and Shepson (2005) for butane:
  - 1-nitrate ≈ 2-nitrate
- Also work from T. Cox (Cassanelli et al., 2007):



1-pentyl 7%



2-pentyl 11%

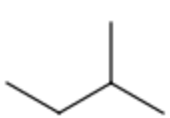
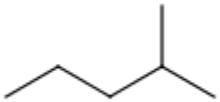
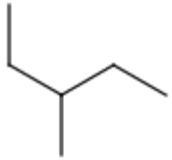


2-methyl-2-butyl 11%

- Wennberg group: isoprene nitrate yields independent of isomer

Scope of This Work

- Series of linear and branched alkanes
- Butane, pentane, cyclohexane
- Isopentane, 2-methyl pentane, 3-methyl pentane…

- Explore both absolute and relative (internal) yields

- Experiments in the presence of pentane also used for relative yields

- NB: To normalize yields, need fractional site of attack – SAR

Apparatus

- Experiments done in 47-Liter steel chamber
- Photolysis using a filtered Xe-Arc lamp (at end of chamber)
- Temperature of chamber can be varied from 230 K to 350 K

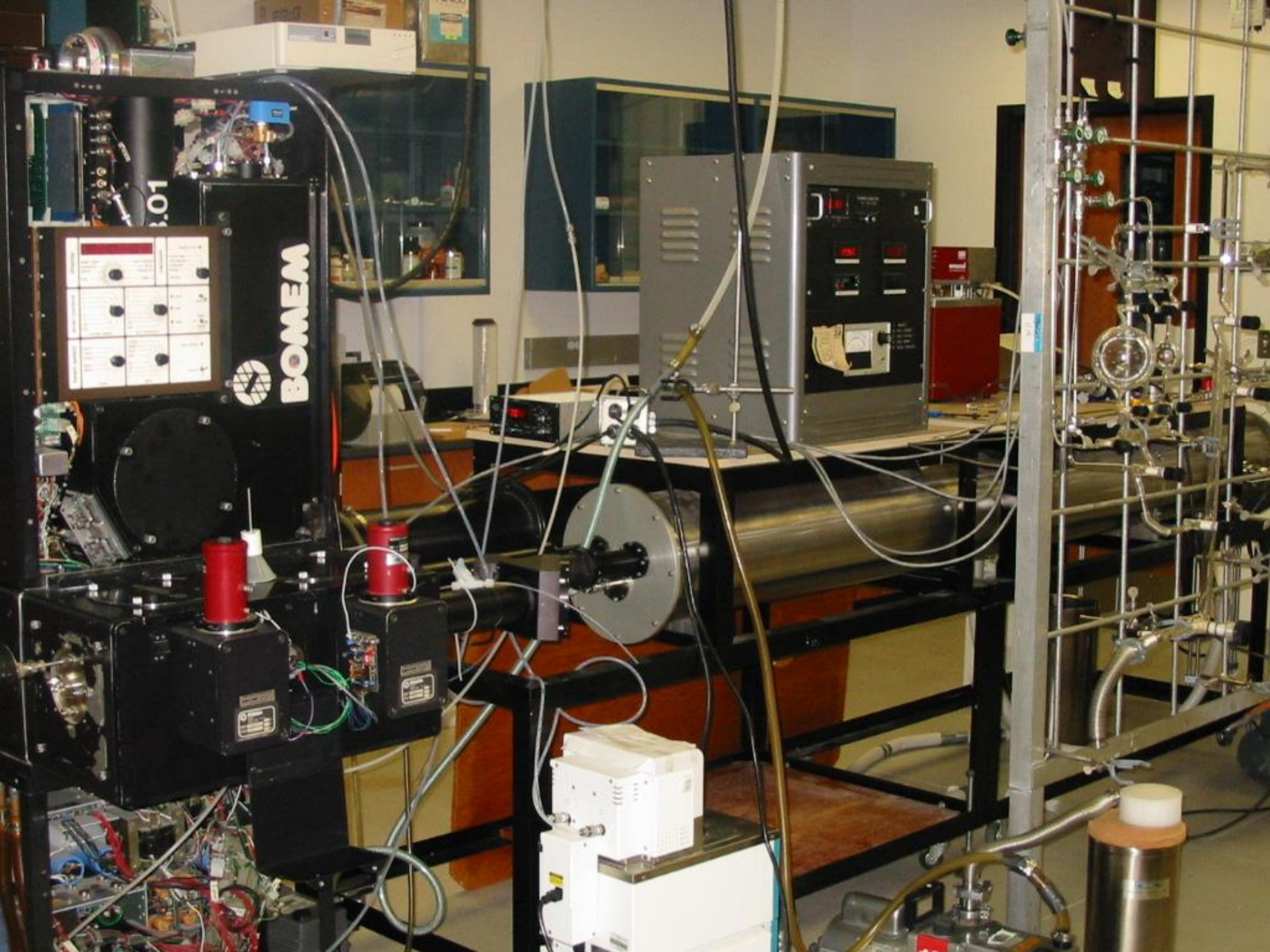
- React alkane(s) with OH (or Cl) in the presence of NO

- Experiments done at 720-800 Torr

- Detection using FTIR and GC-FID (alkanes, NOx, prods)

- Room temperature GC sampling loop to reduce losses

- Can detect nitrates, also major carbonyl products


BOMEM

Nitrates used as standards

- Synthesized 6-8 nitrates, bought 3
- Purified 3 of home-made nitrates

- Between home-made and bought nitrates, able to show that nitrates have same response in FTIR, and Carbon-dependent response in GC-FID
  - (roughly N-0.7 C-atoms)
  - Agrees Atkinson et al. (pers. comm.)

- Assume same response for different isomers

Results: Unbranched Alkanes

- To obtain site-specific yields need SAR for OH+Alkane

- Measured nitrate yields from n-pentane:
- Primary nitrate 1.1%, 2-nitrate 6.7%, 3-nitrate 4.8%
- Site of attack: Prim 9.2%; 2-site 54.2%; 3-site 36.6%

- Normalize for site of attack → 12% , 12% and 13%
- MCM Yields 5.2%, 12.9%, 13.1%

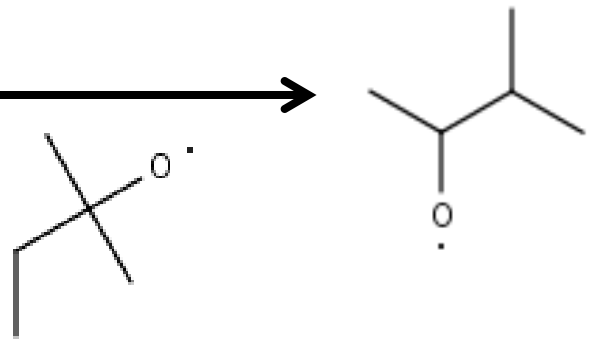
- Yields from cyclohexane (all secondary $–CH_2–$)
- Nitrate 18% (agrees with literature, but MCM 7.8%)

Results: Branched Alkanes

- Isopentane
  - Primary nitrates not fully resolved (but in ratio 2:1)

	Primaries	Secondary	Tertiary
Site of Attack	(10+5)%	29%	56%
Yield	1.4	3.1	7.9
Normalize	9	11	14
MCM/Arey	5.2	14.1	4.7

  - See >55% yield of acetone
  - 3-methyl 2-butoxy must decompose to to 2-propyl radicals
  - MCM rate 4500 s^{-1} (slower than O_2)
  - Vereecken SAR ~1E7 s^{-1}

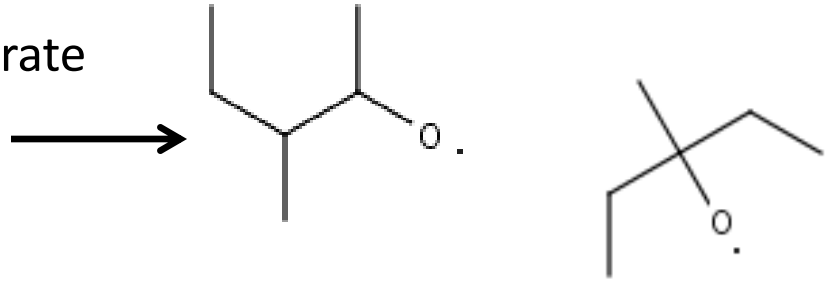


Results: Branched Alkanes

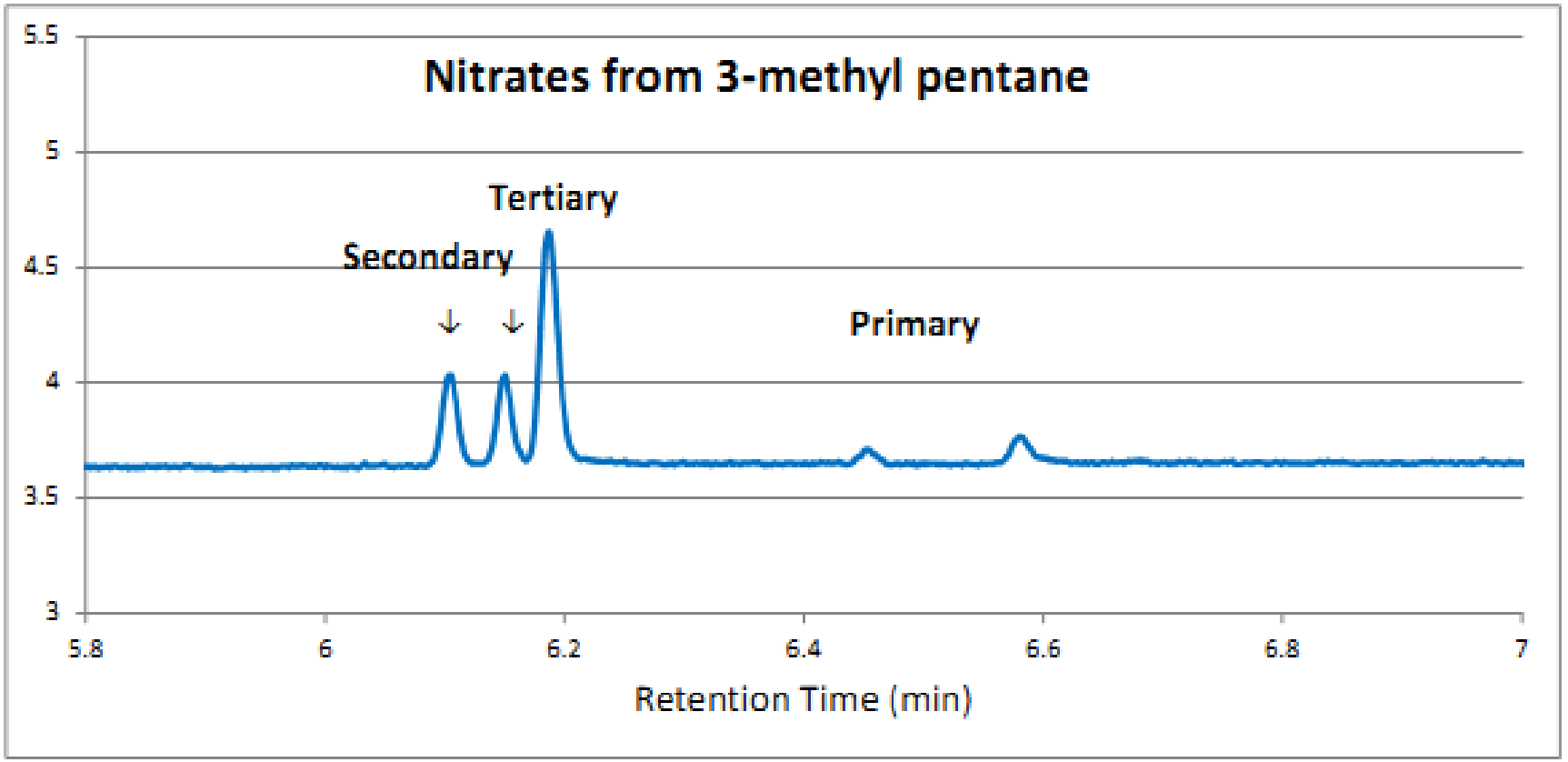
- 3-methyl pentane
  - See 5 peaks: 2 diastereomers from 2-attack (identified by synthesis)

	Primary(1)	Primary(2)	Secondary	Tertiary
Site of Attack	6.6%	3.3%	39%	51%
Yield	1.1	0.5	6.8	9.5
Normalize	17	15	17	18
MCM/Arey	7.8	7.8	17.8	5.9

- Relative to pentane, secondary 1.25x
- See large yield of MEK and 2-butyl nitrate
- Secondary radical must decompose
- MCM isomerization/O_2 rxn



Nitrates from 3-methyl pentane



Results: Branched Alkanes

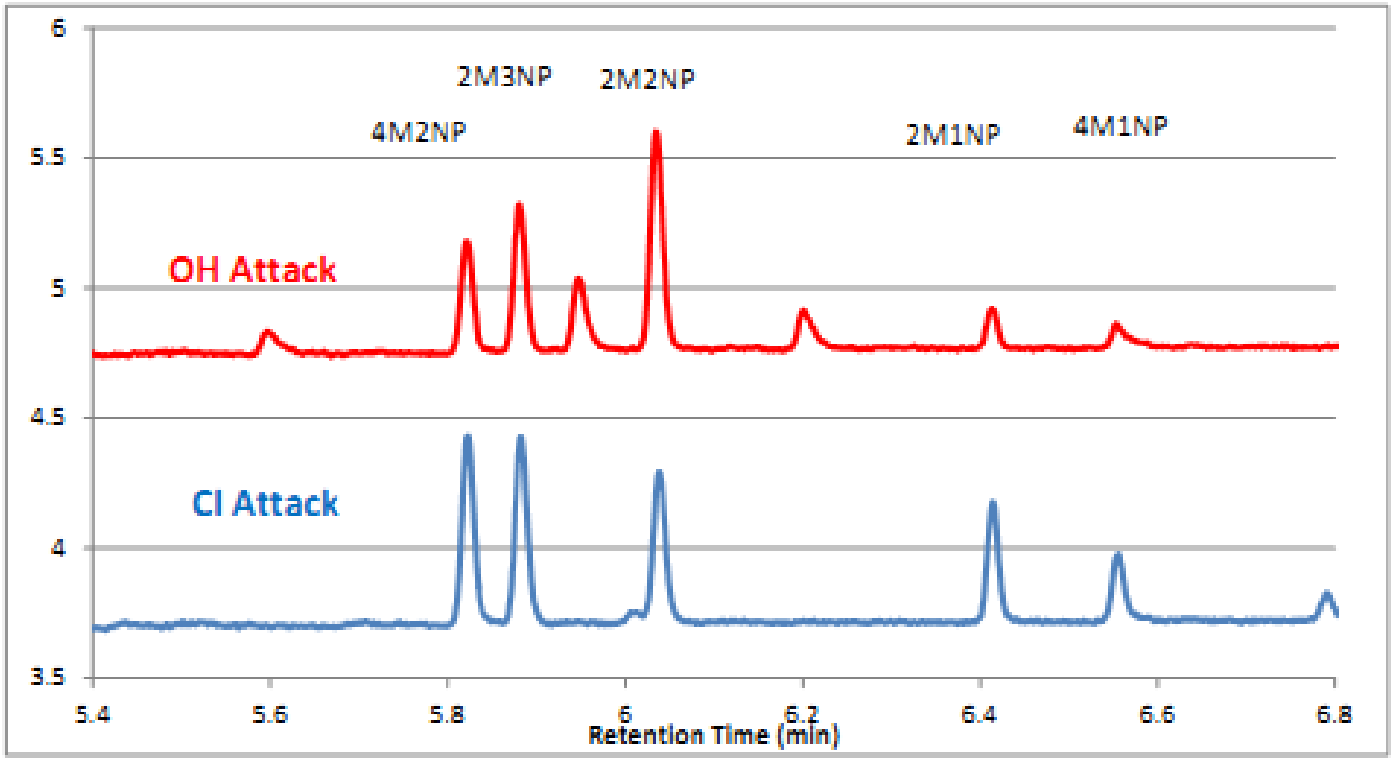
- 2-methyl pentane
  - See 5 peaks: 2 secondary, 1 tertiary, 2 primary

	Primary (1)	Secondary (1)	Secondary (2)	Tertiary
Site of Attack	7%	21%	28%	40%
Yield	1.2	3.8	5.4	7.6
Normalize	18	18	19	19
MCM/Arey	7.8	19.0	19.0	3.1

- Use of OH and Cl identifies tertiary
- One of secondary nitrates prepared by synthesis
- Secondary nitrates relative to pentane 1.30

Nitrates from 2-Methyl pentane

- 2-methyl pentane
  - Multiple peaks
  - Yields from Cl similar all 15-19%, but OH favors tertiary



Some Observations

- Yields of Tertiary and Primary nitrates appear similar to Secondary

- Previous work may have suffered from decomposition or hydrolysis
  - We have observed this with cryotrapping
  - Other groups find tertiary nitrates hydrolyse

- Yields of primary nitrates very low (attack on CH_3) – presumably difficult to measure

Everything looking great?

Of course not!

- Larger, multiply branched alkanes an issue (some of Bernard's outliers)

- 2,4-dimethyl pentane
- Tertiary nitrate only 50% of total
- SAR predicts more like 65%

- Also, SAR predicts rate coefficient to be 6E-12,
- Measured value 4.5E-12 (we checked it!)

An extreme Case

- 3,4-diethyl hexane (= tetra ethyl ethane)

- (Aschmann et al., 2001)
  - SAR 1.25E-11, meas 7.4E-12.
  - Product yields inconsistent with SAR.
  - Predicts ~60% abstraction from tertiary site.
  - Products (3-pentanone) indicate more like 30%.

  - SAR Overpredicting activated tertiary sites?

Conclusions

- Yields of tertiary nitrates comparable to secondary
- Primary nitrates similar (but depend on knowledge of SARs)
- Note that OH attack tends to favor tertiary sites
  - We have been underestimating these by a factor of 2-3

- Product yields suggest that SAR not working for branched alkanes
- This work supported by the National Science Foundation and the Coordinating Research Council