

Identification and Atmospheric Reactions of Polar Products of Selected Aromatic Hydrocarbons (contract no. 03-319)

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- Aromatic hydrocarbons, including PAHs, are present in gasoline and diesel fuels and are emitted in the exhaust from gasoline- and diesel-fueled vehicles.
- The most abundant aromatic compounds are benzene and alkylbenzenes (toluene, the xylenes, ethylbenzene, and 1,2,4-trimethylbenzene) and naphthalene and C₁-C₂ alkylnaphthalenes.

Transformation processes

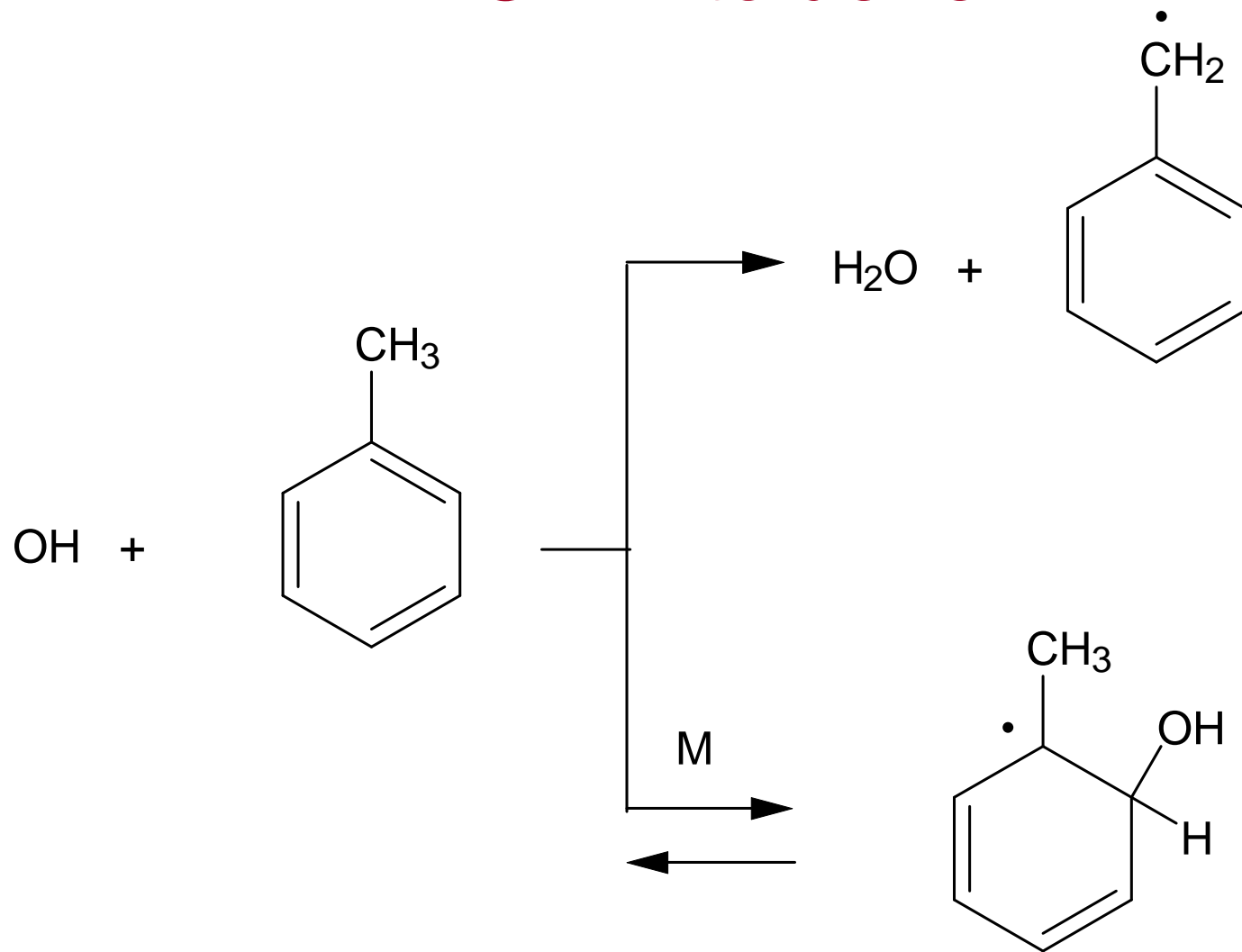
In the troposphere, these monocyclic aromatics and PAHs react in the gas phase with:

- OH radicals during daytime.
- NO₃ radicals during evening and nighttime hours.
- The daytime OH radical reaction is calculated to dominate as their tropospheric loss process.

OH radical reaction

- Kinetic and product studies show that for both monocyclic aromatic hydrocarbons and PAHs, these reactions proceed mainly by initial OH radical addition to the aromatic ring(s) at room temperature and below.
- At elevated temperatures, the reactions proceed by H-atom abstraction.

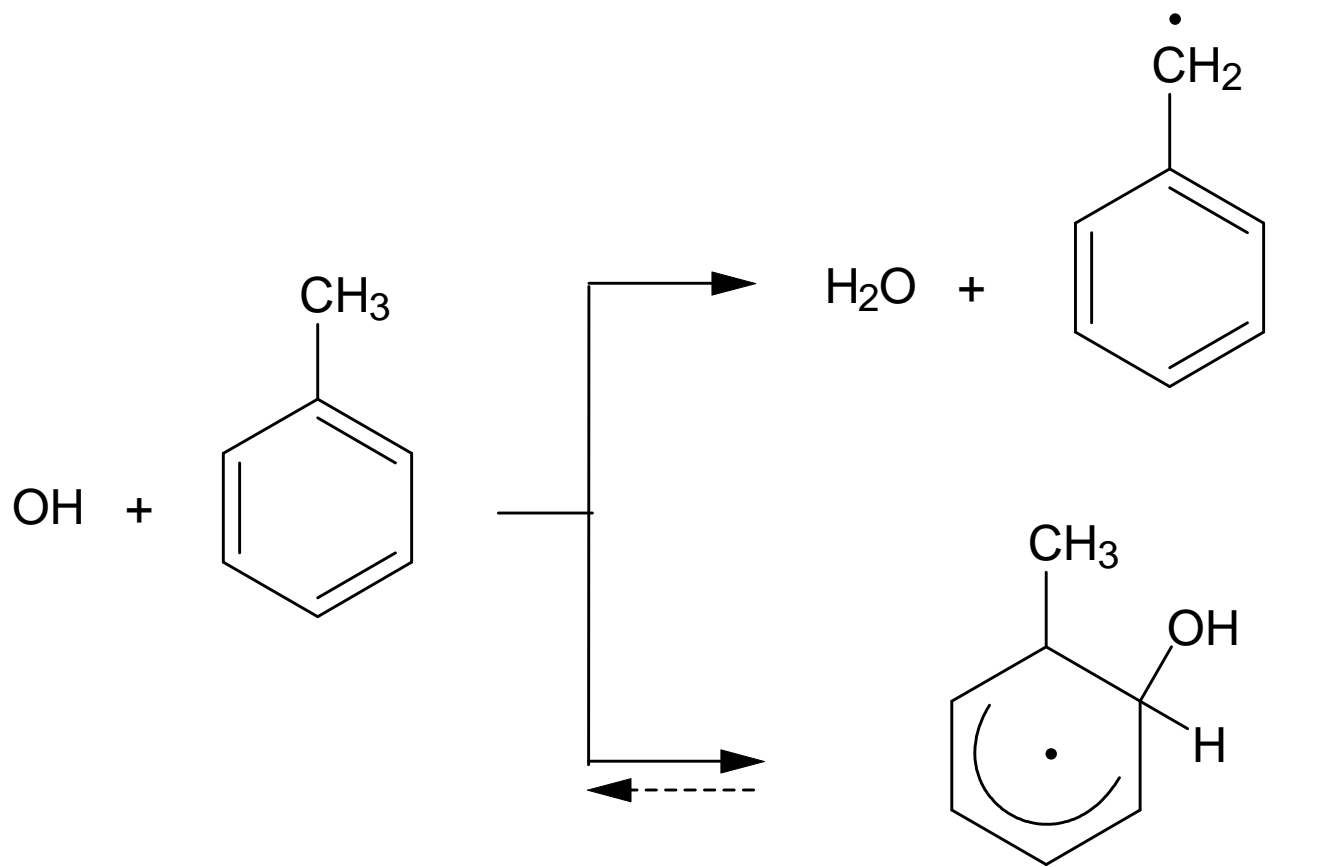
OH + toluene



OH-aromatic (or OH-PAH) adduct

Reactions of OH-aromatic adducts

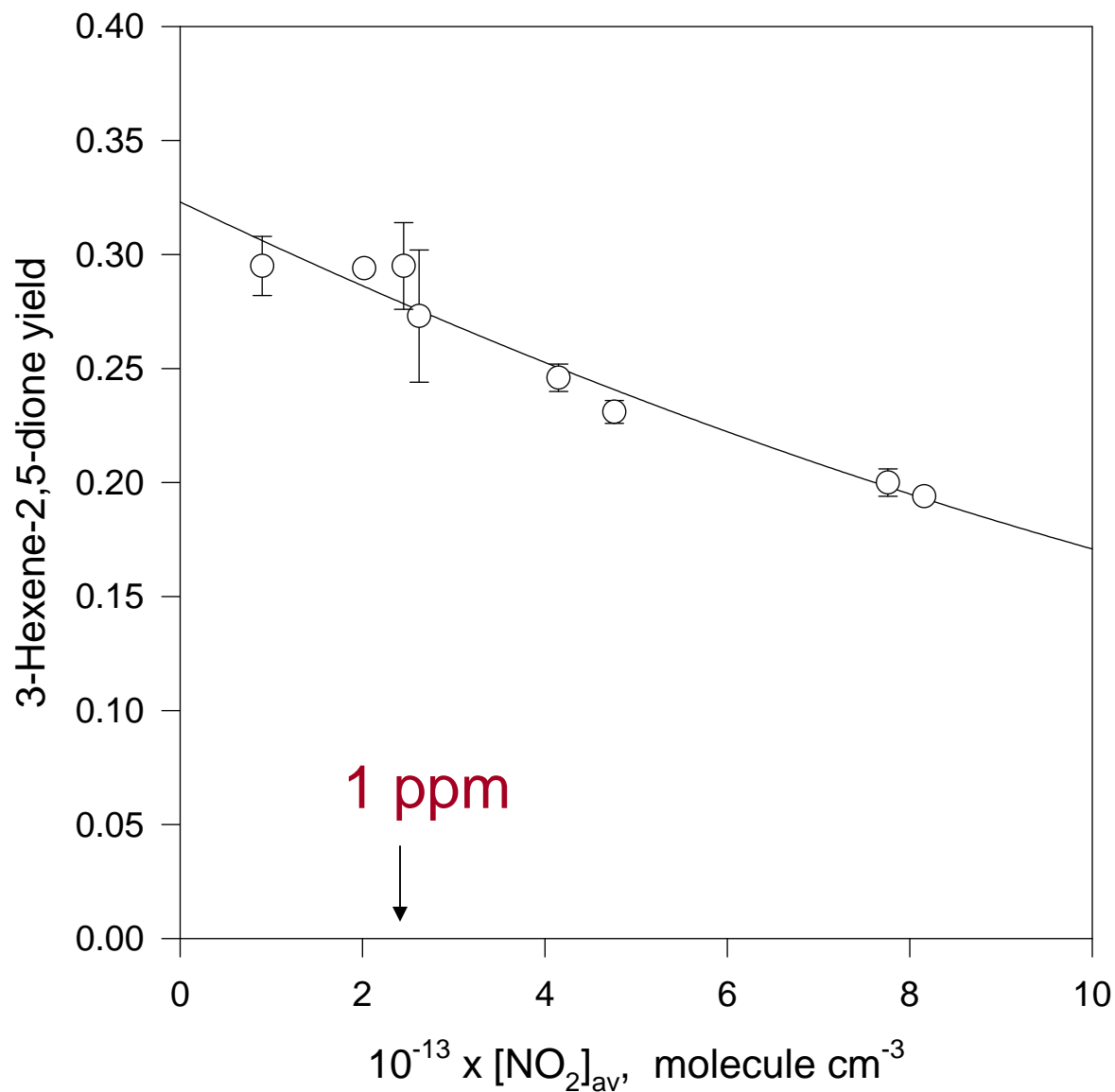
- For benzene, toluene and the xylenes, the OH-aromatic adducts react with O_2 and NO_2 , with these reactions being of equal importance in air at 1.1 ppm NO_2 for benzene, 3.3 ppm NO_2 for toluene and 8-13 ppm NO_2 for the xylenes.
- Under ambient atmospheric conditions, the OH-monocyclic aromatic adducts react dominantly with O_2 .
- However, the observation in ambient air of nitro-PAH formed from gas-phase OH radical-initiated reactions suggests that the OH-PAH adducts react to a significant extent with NO_2 under ambient atmospheric conditions.



Products, including
ring-cleavage dicarbonyls

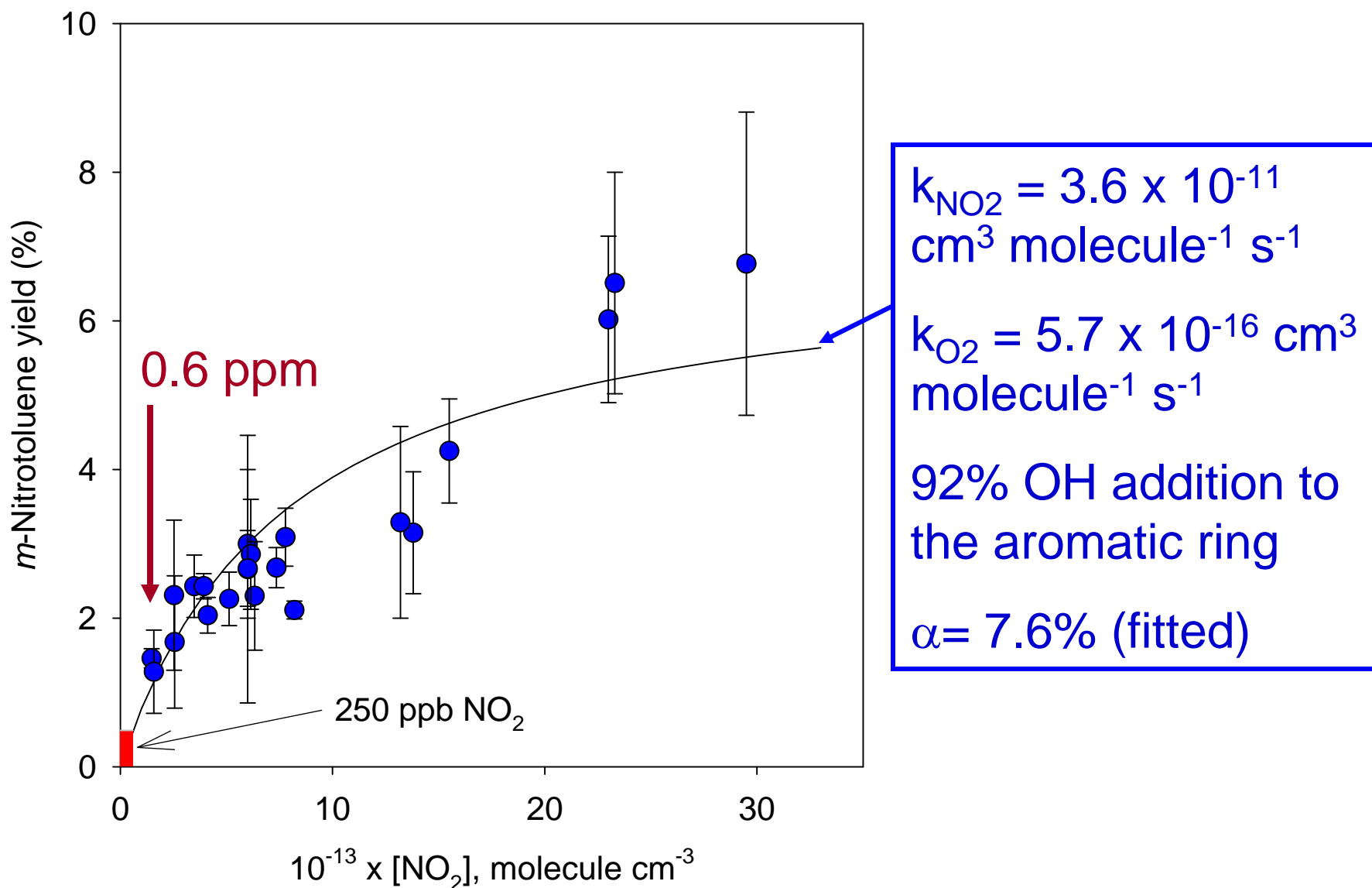
Products, including
nitro-aromatics

Formation of 3-hexene-2,5-dione from OH + *p*-xylene as a function of [NO₂]



From Bethel
et al., 2000

3-Nitrotoluene yields from OH + toluene (data from Atkinson *et al.*, 1989)



Specific tasks carried out

1. Investigation of ring-cleavage dicarbonyls from the OH radical-initiated reactions of monocyclic aromatic hydrocarbons.
2. Develop a reliable and convenient *in situ* source of glyoxal for routine quantitative calibration of analysis methods.
3. Investigation of ring-cleavage dicarbonyls from the OH radical-initiated reactions of selected PAHs.
4. Investigation of nitro-aromatic and nitro-PAH formation yields from the OH radical-initiated reactions as a function of NO₂ concentration.

1. Carbonyl products from OH + monocyclic aromatic hydrocarbons

- Investigated the formation of 1,2- and unsaturated 1,4-dicarbonyls from the OH radical-initiated reactions of toluene, the xylenes and the trimethylbenzenes.
- OH radicals generated by:





Experiments carried out in 7000 liter Teflon chamber.

Initial concentrations of aromatic, CH_3ONO and NO , ~ 1 ppm each.

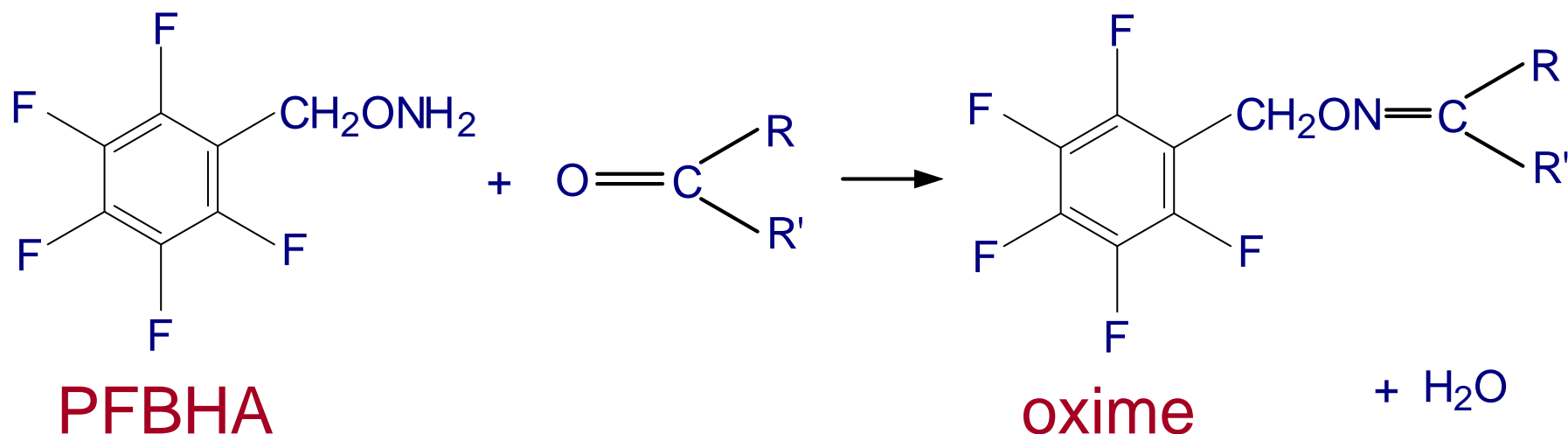
20-30% of initial aromatic consumed by reaction.

Final NO_2 concentration 0.4-0.9 ppm.

- Aromatic hydrocarbon concentrations measured by GC-FID. Samples collected onto Tenax solid adsorbent, with subsequent thermal desorption and GC-FID analysis.
- Carbonyl products measured by Solid Phase MicroExtraction fibers pre-coated with a derivatizing agent for on-fiber derivatization, with subsequent thermal desorption and analysis by GC-MS.

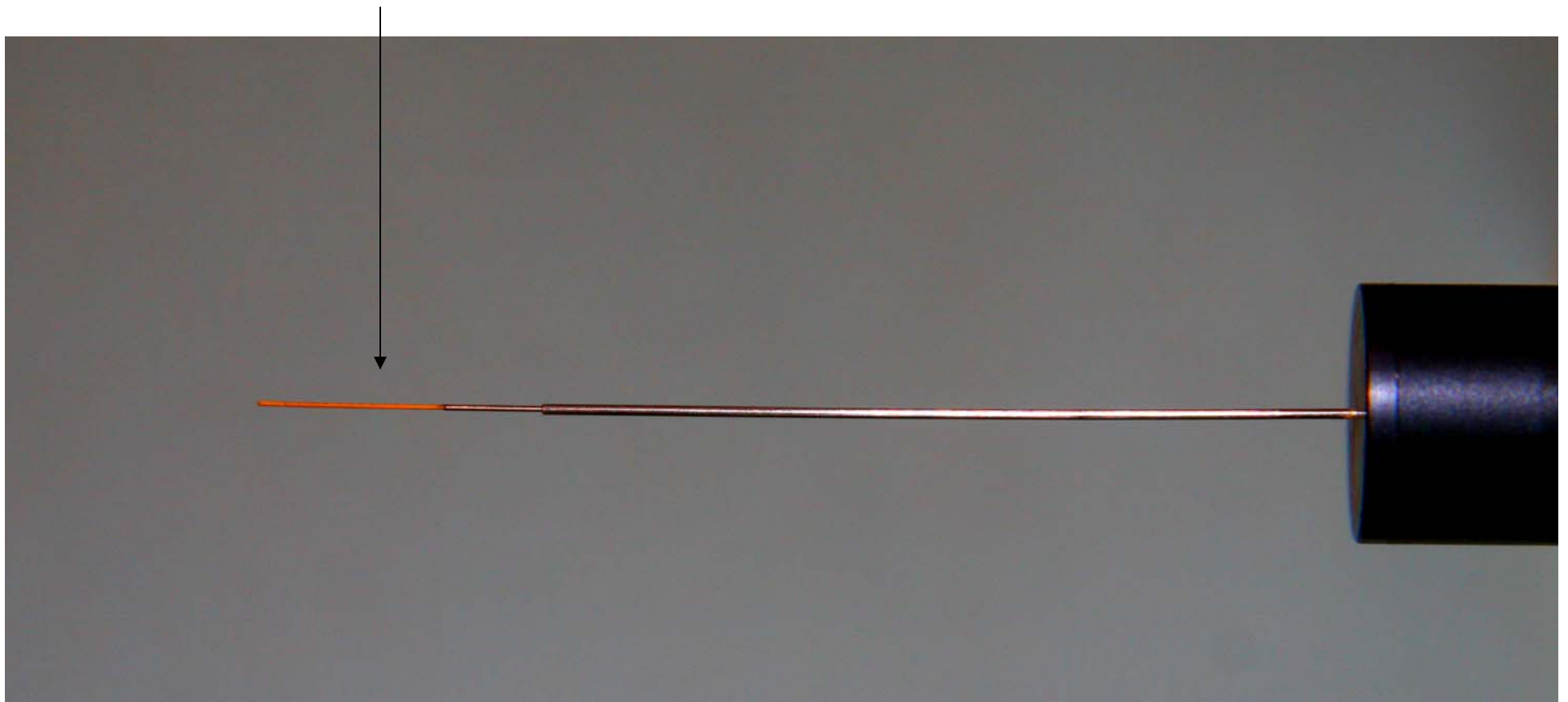
Solid-Phase MicroExtraction fibers

Pre-coated with *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) for on-fiber derivatization of carbonyl-containing compounds.



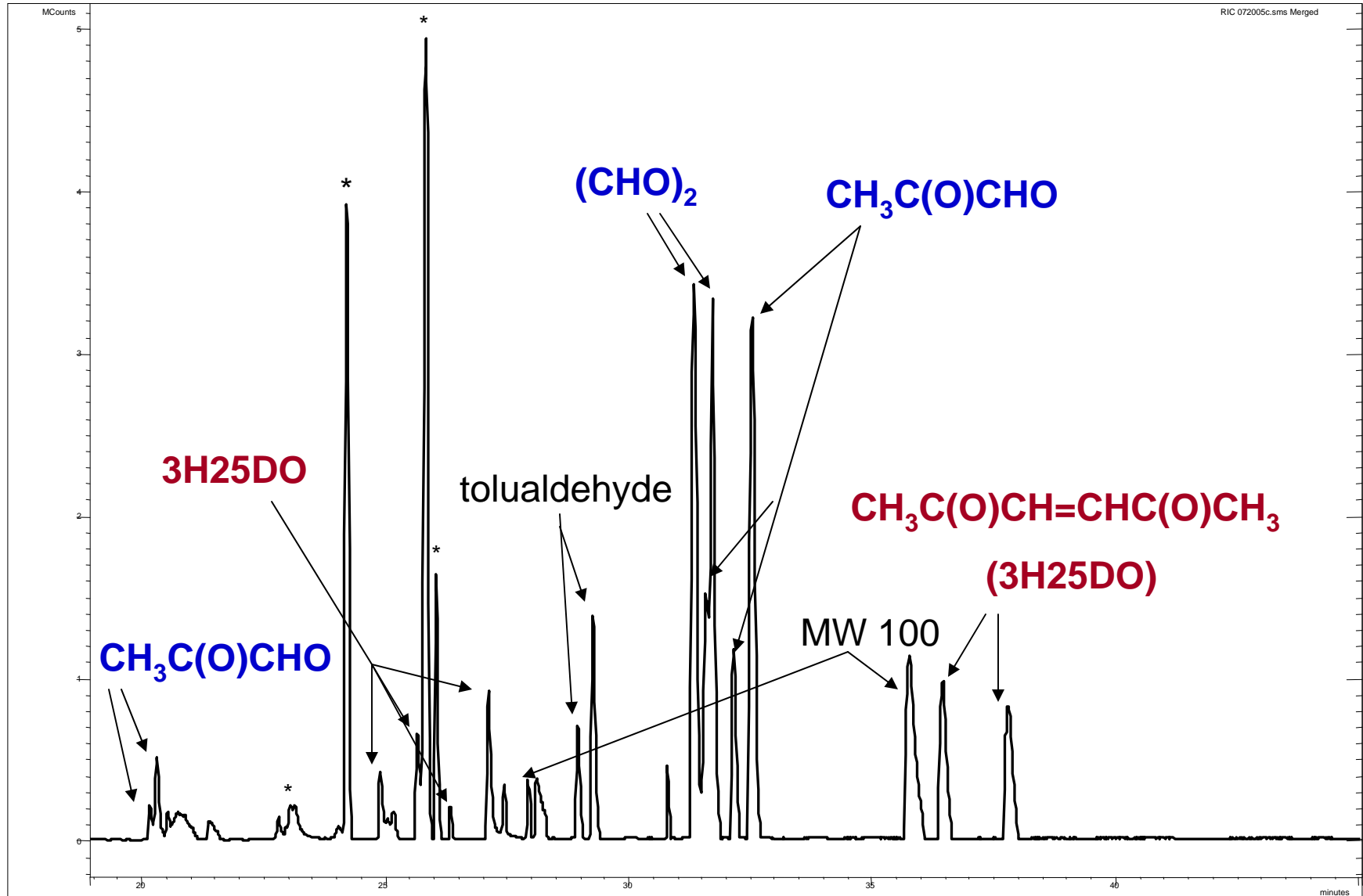
Fibers are retractable. After coating with PFBHA, the fibers are exposed to the chamber contents with the chamber mixing fan on for typically 5 min.

Fiber, ~20 mm long



OH + *p*-Xylene

Chromatogram Plot

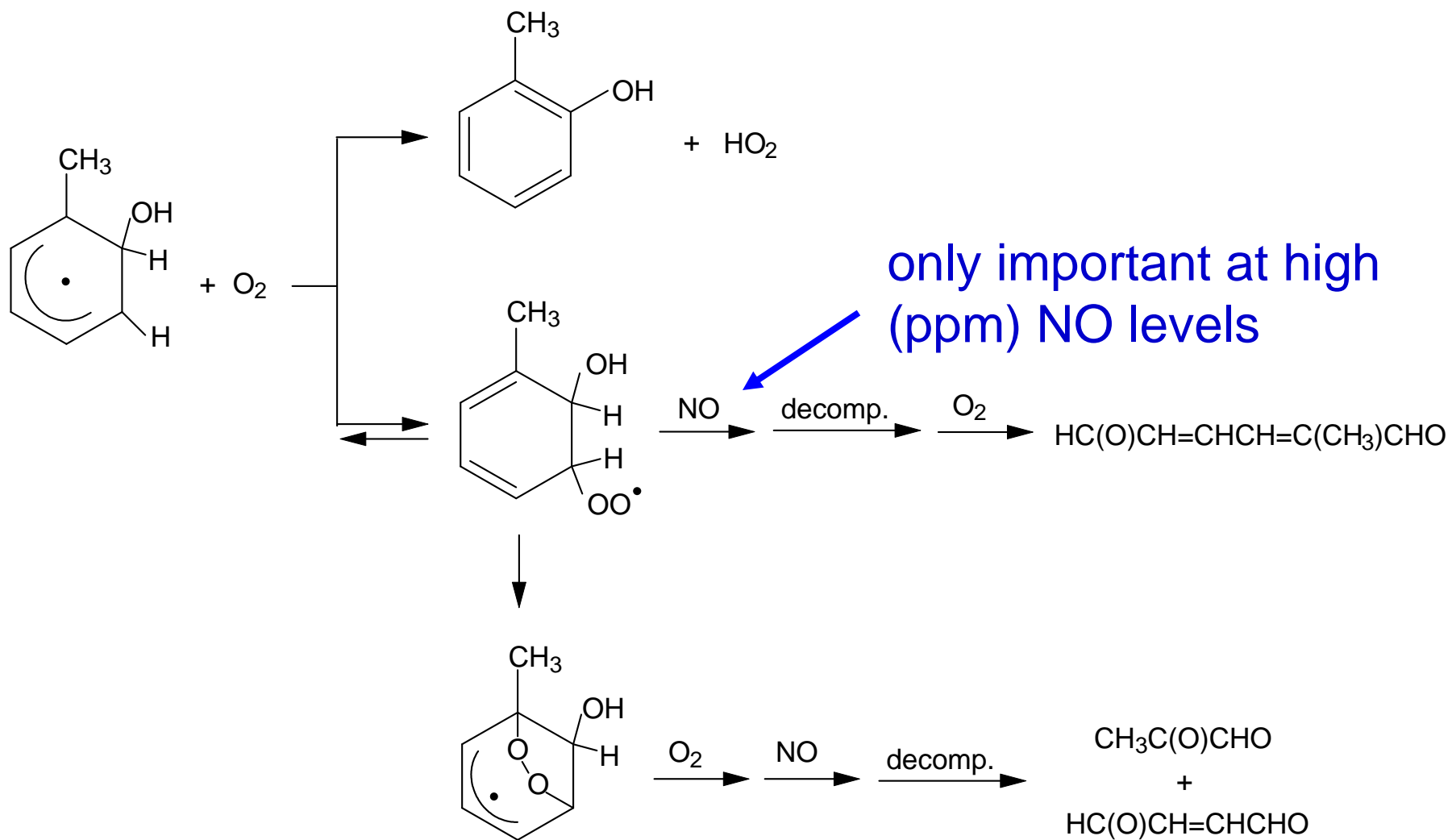


ring-opened product	toluene	xylene			trimethylbenzene		
		<i>o</i> -	<i>m</i> -	<i>p</i> -	1,2,3-	1,2,4-	1,3,5-
(CHO) ₂	X	X	X	X	X	X	
CH ₃ C(O)CHO	X	X	X	X	X	X	X
CH ₃ C(O)C(O)CH ₃		X			X	X	
HC(O)CH=CHCHO	X	X					
CH ₃ C(O)CH=CHCHO	X	X	X		X		
CH ₃ C(O)C(CH ₃)=CHCHO		X			X	X	
CH ₃ C(O)CH=CHC(O)CH ₃				X		X	
CH ₃ C(O)CH=C(CH ₃)CHO							X

Dicarbonyls from OH + monocyclic aromatics

- All possible 1,2-dicarbonyls (glyoxal, methylglyoxal and biacetyl) are observed. Biacetyl is only formed from *o*-xylene and 1,2,3- and 1,2,4-trimethylbenzene.
- A series of unsaturated 1,4-dicarbonyls are observed (but not all possible ones).
- 3-Hexene-2,5-dione ($\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CHC}(\text{O})\text{CH}_3$) is only formed from *p*-xylene and 1,2,4-trimethylbenzene.
- These data are qualitative.
- 3-Hexene-2,5-dione can be analyzed by GC without prior derivatization. At low NO_2 concentrations the 3-hexene-2,5-dione formation yield from OH + *p*-xylene is identical to that of the potential co-product glyoxal (Bethel *et al.*, 2000; Volkamer *et al.*, 2001, 2005).
- Yields of 1,2-dicarbonyls and, if possible, unsaturated 1,4-dicarbonyls are needed as a function of $[\text{NO}_2]$.

Proposed reaction scheme for OH-toluene adduct + O₂



2. Source of glyoxal for routine calibration

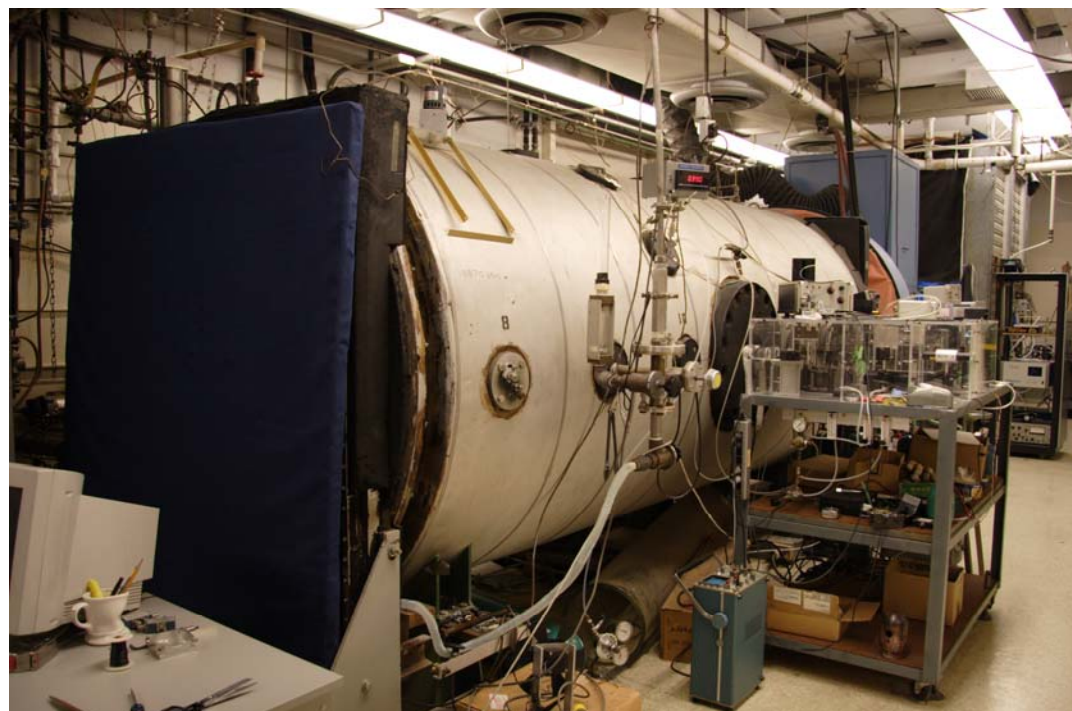
- Glyoxal, $(\text{CHO})_2$, is available as a hydrate and is difficult to prepare pure in the gas phase.
- Use a gas-phase reaction to generate known amounts of glyoxal.
- $\text{OH} + (\text{CH}_3)_2\text{C}=\text{CHCHO}$ (3-methyl-2-butenal) was chosen as a candidate.



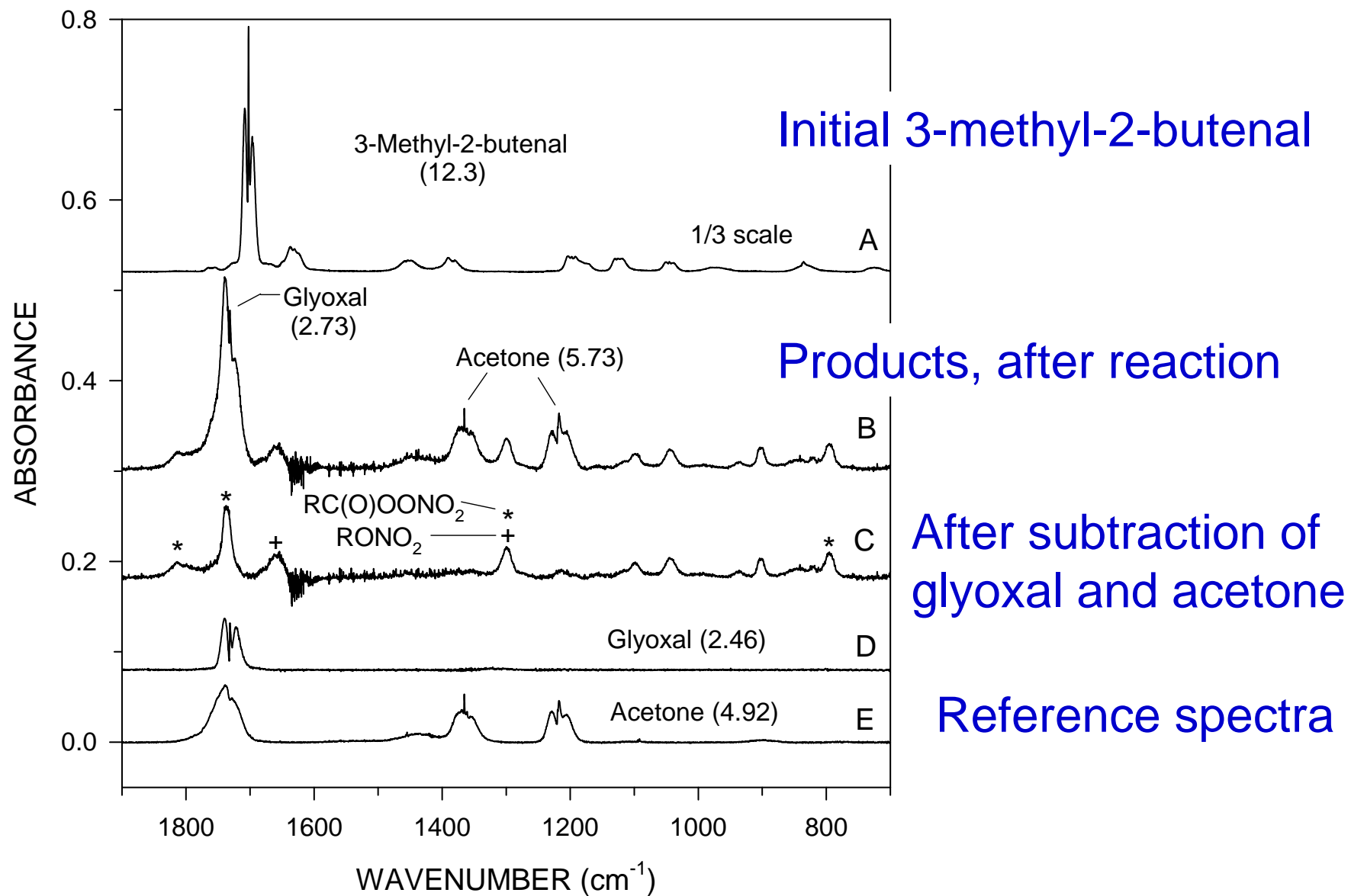
- Measured OH radical reaction rate constant of 3-methyl-2-butenal; $k = 6.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $296 \pm 2 \text{ K}$. 7000 liter Teflon chamber used, with GC-FID analyses
- Investigated products using *in situ* FT-IR spectroscopy in 5870 liter evacuable chamber.
- Additionally, the formation of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CHO}$ was observed using coated-SPME/GC-FID analyses, and a formation yield of $4.6 \pm 0.7\%$ measured.



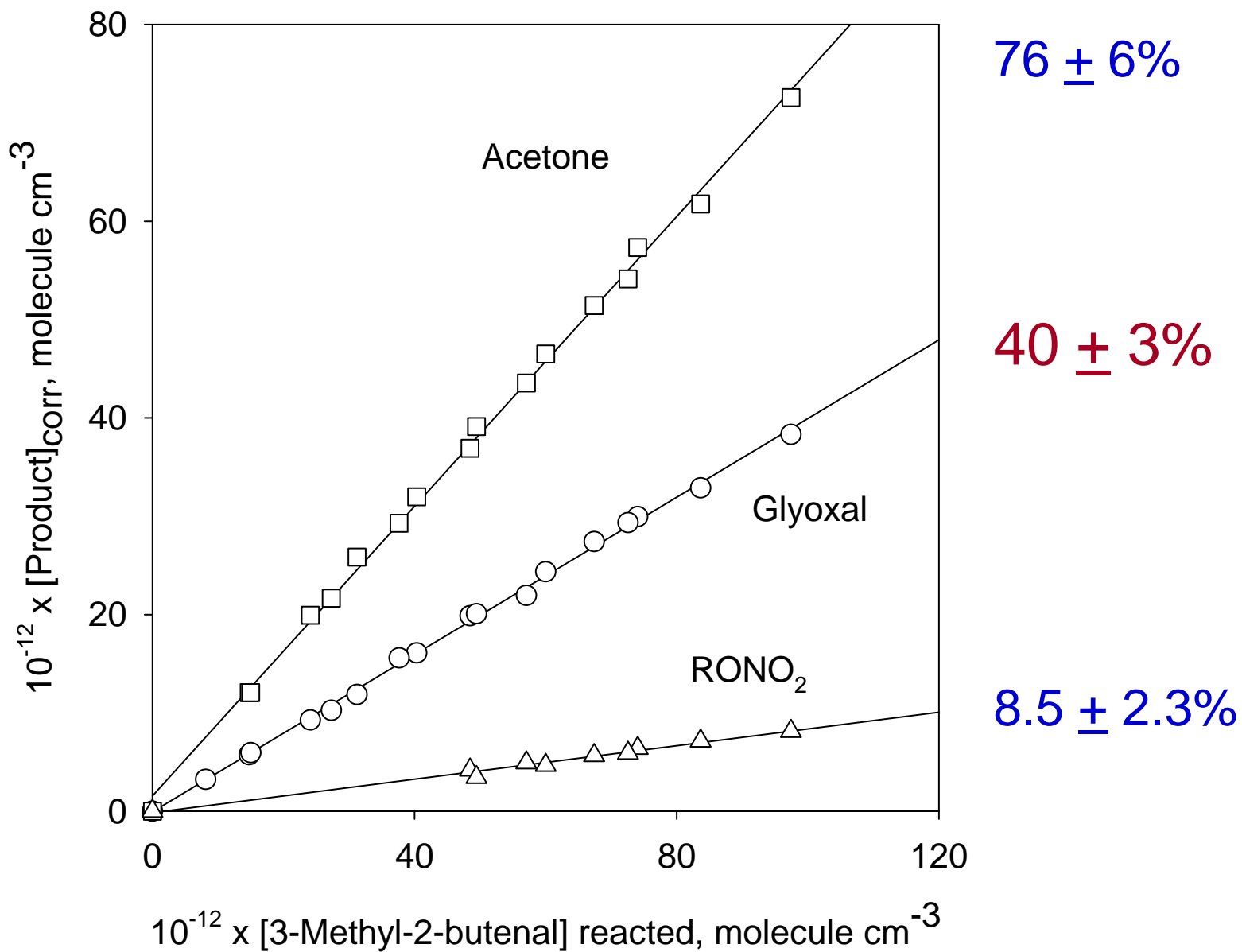
5870 liter evacuable chamber interfaced to an FT-IR spectrometer

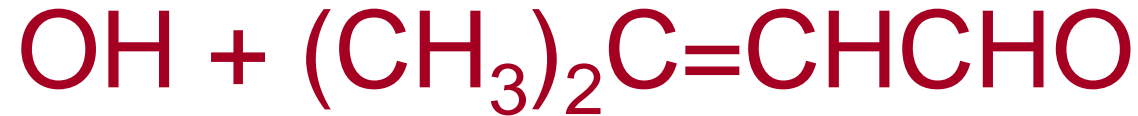


OH + 3-methyl-2-butenal: FT-IR spectra



Formation yields from FT-IR analyses

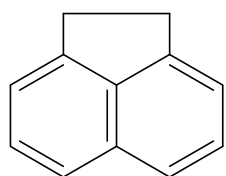




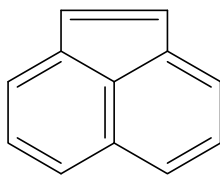
- Glyoxal is formed in $40 \pm 3\%$ yield.
- 3-Methyl-2-butenal is a factor of 5.6 more reactive towards OH radicals than is glyoxal; secondary reaction of glyoxal with OH radicals is hence minor during the reactions.
- $\text{OH} + (\text{CH}_3)_2\text{C}=\text{CHCHO}$ is a good *in situ* source of glyoxal for routine calibration purposes.

3. Formation of glyoxal and selected dicarbonyls from OH + PAHs

- Glyoxal formation from OH + acenaphthene and acenaphthylene.
- Glyoxal and phthaldialdehyde from OH + naphthalene.
- Glyoxal and 2-acetylbenzaldehyde from OH + 1-methylnaphthalene.
- Glyoxal and 1,2-diacetylbenzene from OH + 1,4-dimethylnaphthalene.

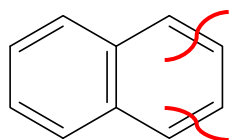


Acenaphthene

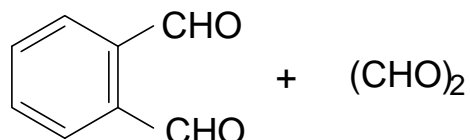
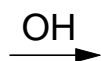


Acenaphthylene

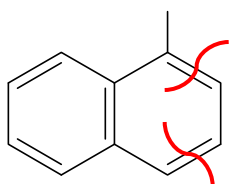
Glyoxal yields



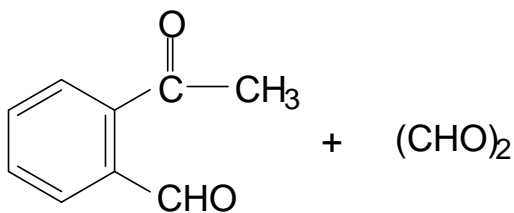
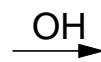
Naphthalene



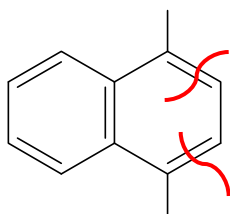
Phthalaldehyde



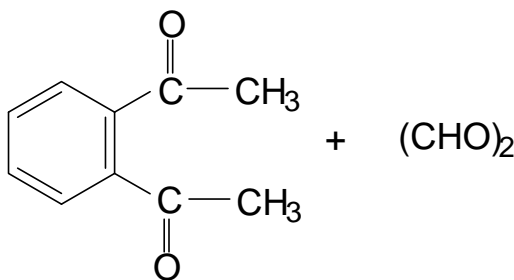
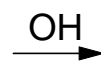
1-Methylnaphthalene



2-Acetylbenzaldehyde



1,4-Dimethylnaphthalene

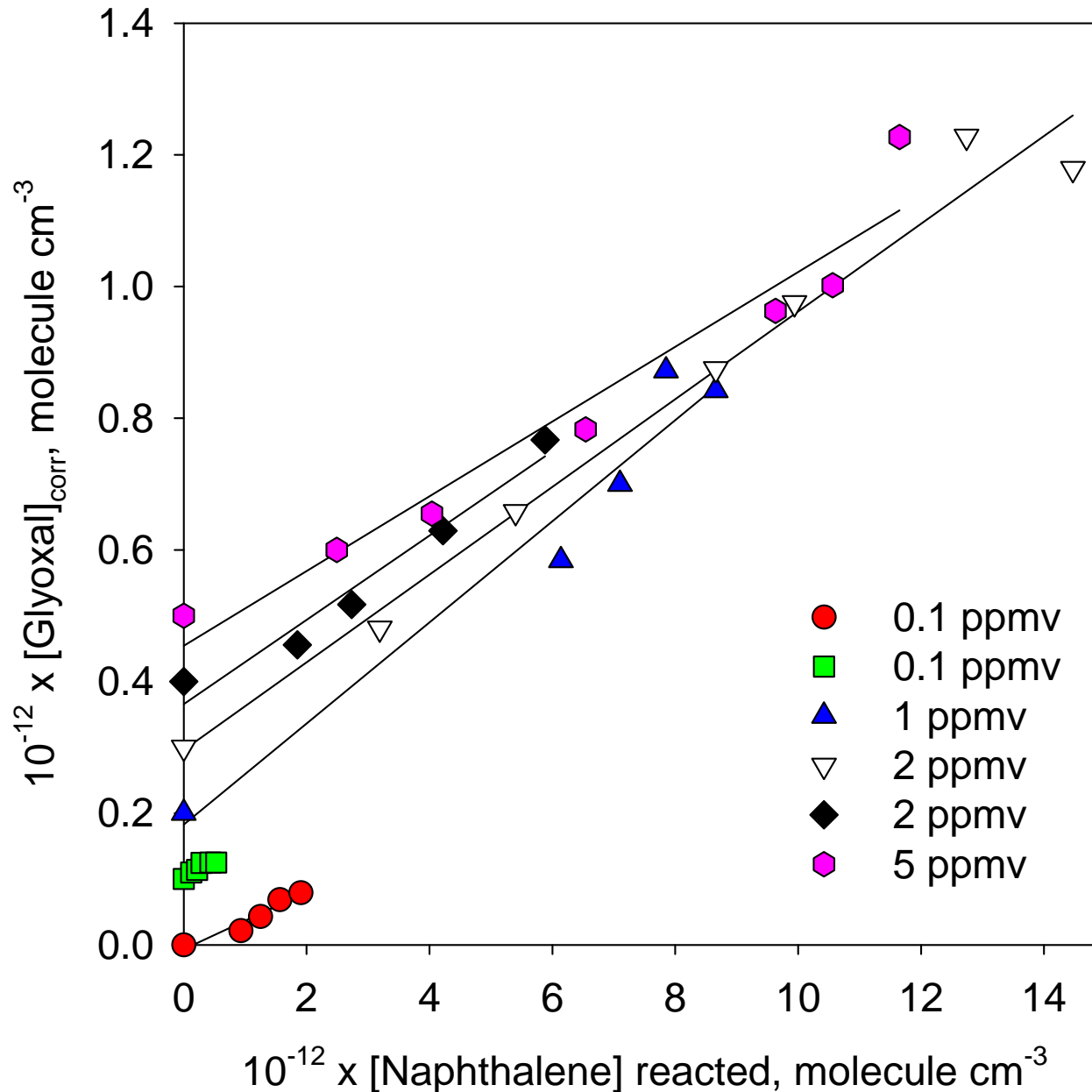


1,2-Diacetylbenzene

Glyoxal yields measured. Are the aromatic dicarbonyl yields the same as those for glyoxal?

- Experiments carried out in 7000 liter Teflon chamber.
- OH radicals generated by photolysis of CH_3ONO or, at low NO_x or in absence of NO_x , by the dark $\text{O}_3 + 2\text{-methyl-2-butene}$ reaction.
- PAH measured by GC-FID after collection onto Tenax solid adsorbent.
- Glyoxal by coated SPME/GC-FID, with calibrations using the $\text{OH} + (\text{CH}_3)_2\text{C}=\text{CHCHO}$ reaction to generate known amounts of glyoxal.
- Aromatic dicarbonyl by SMPE/GC-FID.

Glyoxal from OH + naphthalene

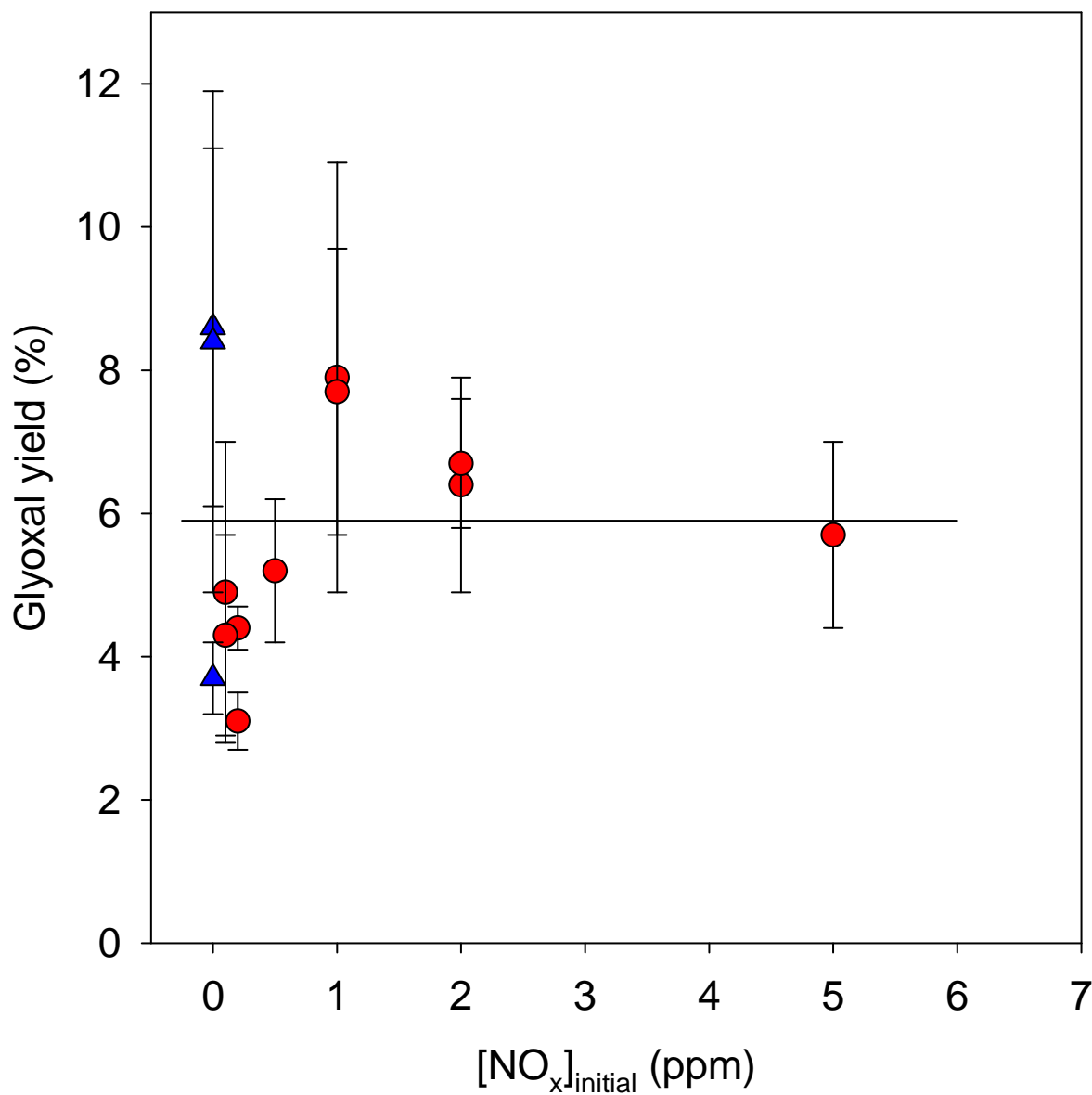


Note:

Most data offset vertically for clarity.

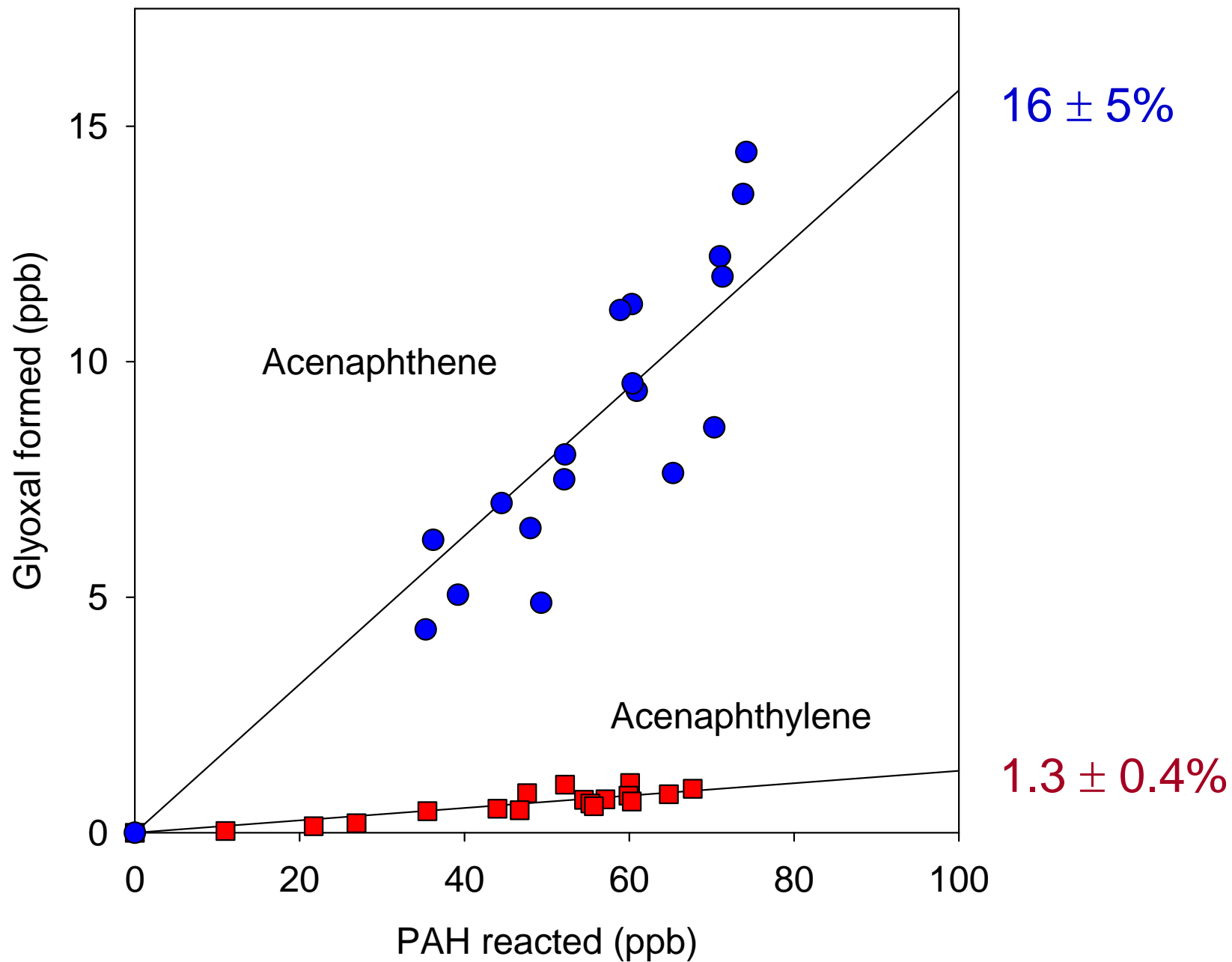
Maximum glyoxal formed was 35 ppb.

- OH from photolysis of CH_3ONO
- ▲ OH from dark $\text{O}_3 + 2\text{-methyl-2-butene}$ reaction



Glyoxal yield
 $= 6 \pm 2\%$,
independent
of initial NO_x

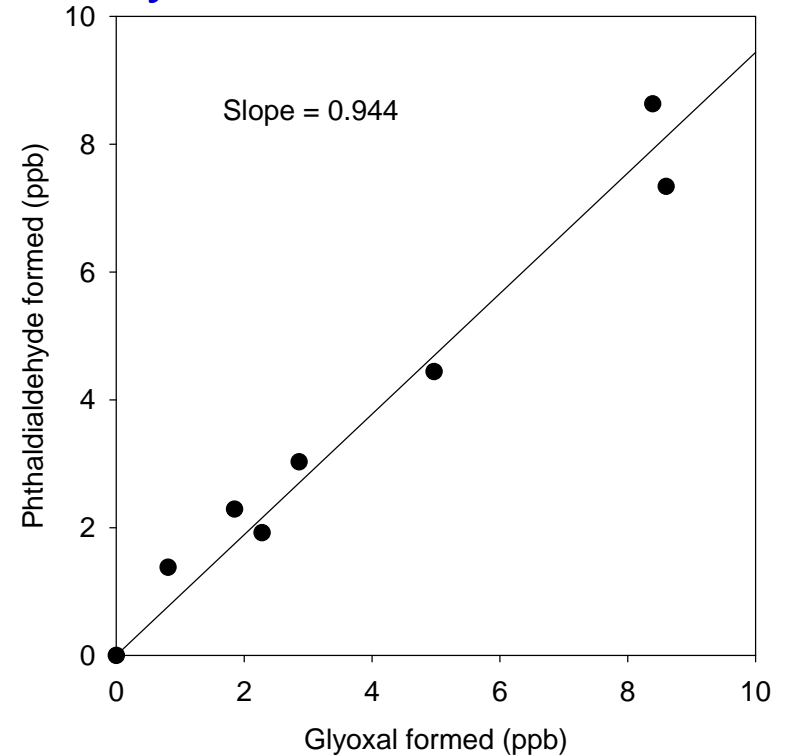
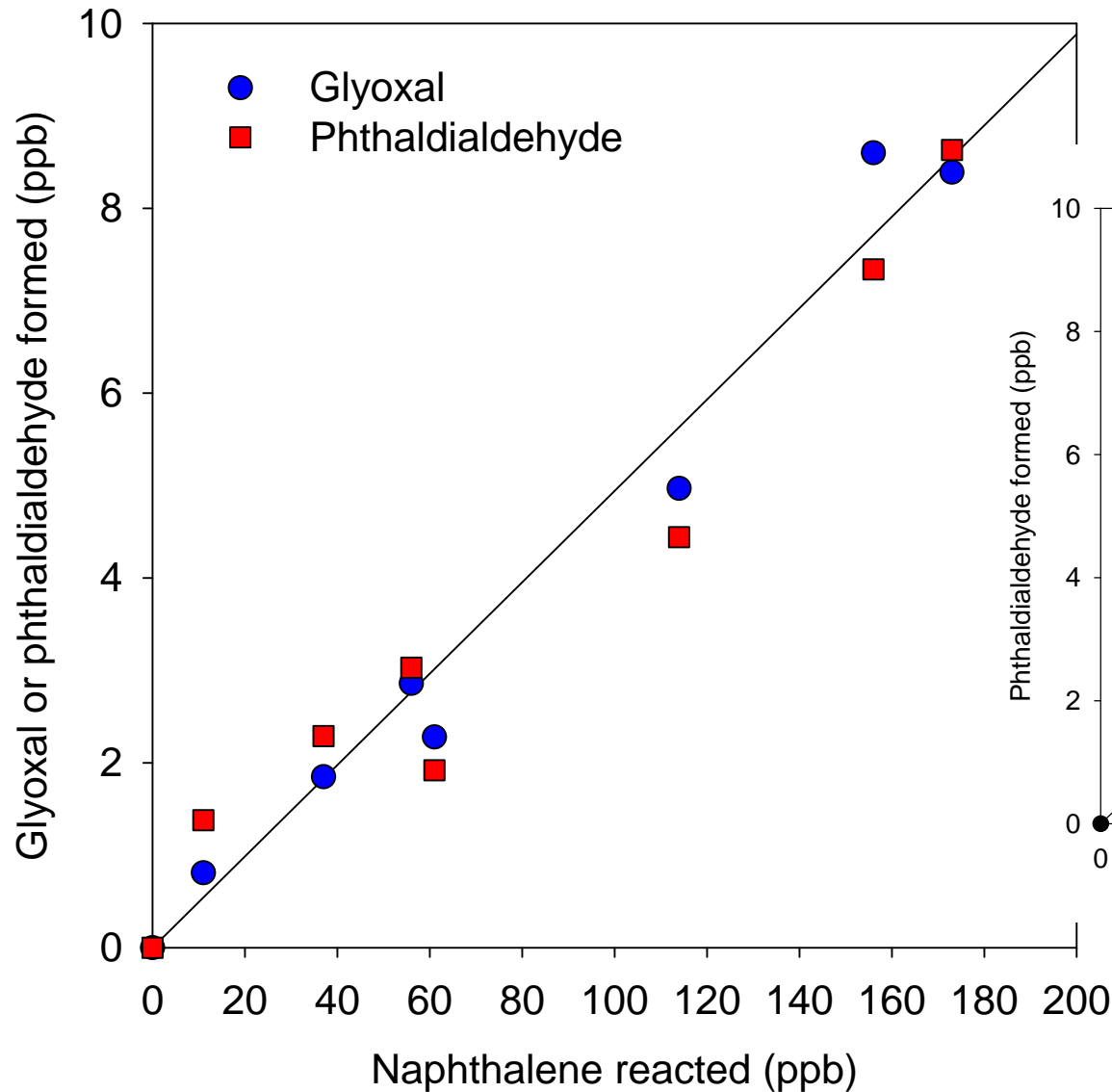
OH + acenaphthene and acenaphthylene; initial NO_x = 0.2-5 ppm



OH + naphthalene, initial $\text{NO}_x = 0.2\text{-}5$ ppm

Glyoxal yield = 4.9%

Phthaldialdehyde yield = 4.7%



PAH	glyoxal (%)	dicarbonyl coproduct (%)
acenaphthene	16 ± 5	
acenaphthylene	1.3 ± 0.4	
naphthalene	6 ± 2 4.9 ± 1.5	4.7 ± 1.5
1-methylnaphthalene	4.1 ± 1.5	$6.8 \pm 2^*$
1,4-dimethylnaphthalene	4.4 ± 1.5	$6.1 \pm 2^*$

*Likely upper limit due to losses during calibration in chamber

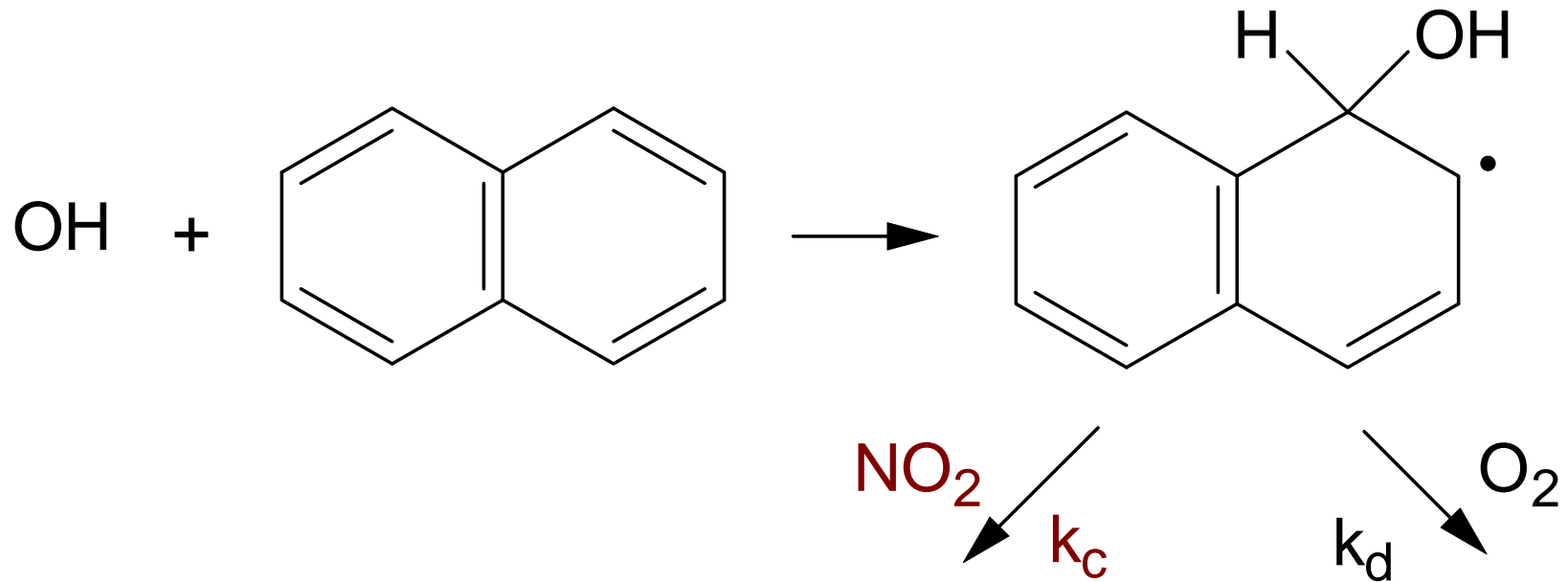
Glyoxal and potential co-product formation

- Glyoxal is a product from OH + acenaphthene and (very minor) from acenaphthylene.
- Glyoxal is a relatively minor product from OH + naphthalene and selected alkylnaphthalenes. Within the experimental uncertainties, the corresponding aromatic dicarbonyl is formed with the same yield as glyoxal, indicating they are co-products.
- For the NO_x concentrations used here, the dominant reactions of the OH-naphthalene and OH-alkylnaphthalene adducts are with NO₂.
- The major pathway of these reactions appears to be ring cleavage to form 2-formylcinnamaldehyde (≥30-35%) from naphthalene and homologous dicarbonyls from other alkylnaphthalenes (CARB contract no.03-314).

4. Nitro-aromatic formation from OH radical-initiated reactions of selected aromatic hydrocarbons

- As noted, nitro-aromatic formation from monocyclic aromatics (benzene, toluene, xylenes) is a function of the NO_2 concentration and approaches zero at ambient NO_2 levels.
- However, the nitro-PAHs formed from OH radical-initiated reactions of PAHs conducted in the laboratory are observed in ambient air at concentrations consistent with yields measured in the laboratory at high (>1 ppm) NO_2 concentrations.

General mechanism



nitroaromatic
(yield = α)

$$\text{Nitroaromatic yield} = \alpha \frac{k_c[\text{NO}_2]}{k_c[\text{NO}_2] + k_d[\text{O}_2]}$$

Nitro-aromatic yields from OH + toluene, naphthalene and biphenyl as a function of NO₂

- Experiments carried out in a 7500 liter Teflon chamber. OH radicals formed by:

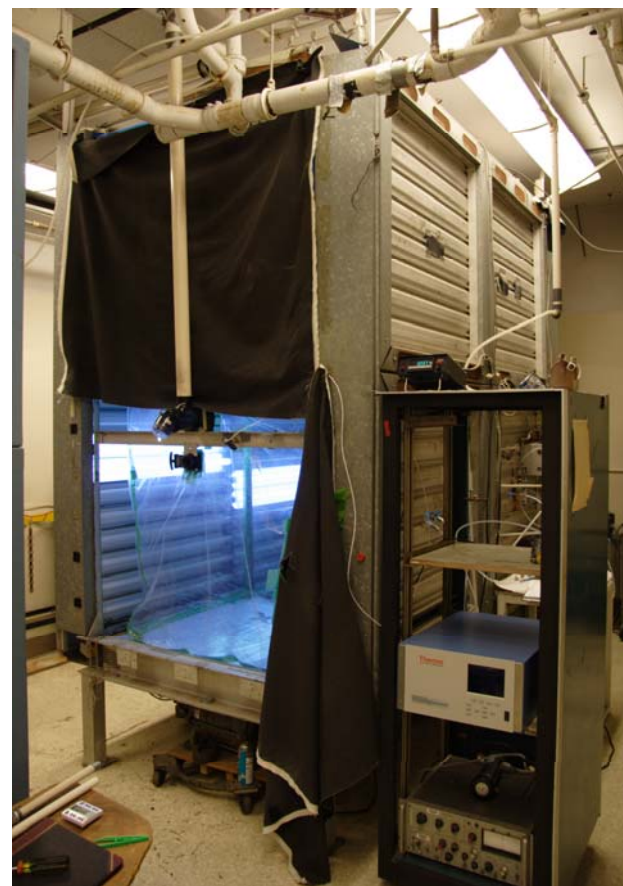
NO₂ ≥ 0.1 ppm:



NO₂ ≤ 0.2 ppm:

from O₃ + 2-methyl-2-butene reaction in the dark.

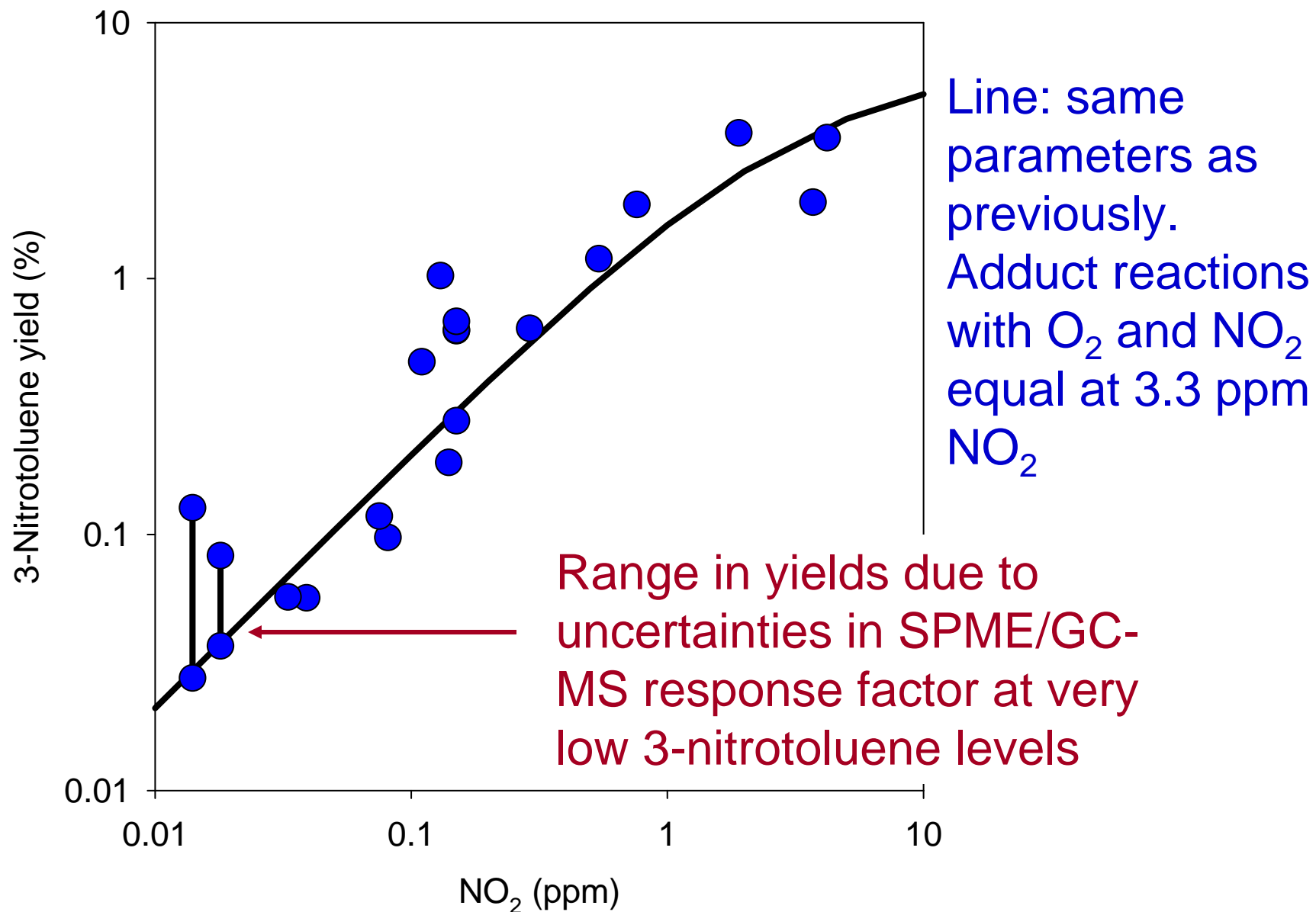
- Analyses by GC-FID and GC/MS.



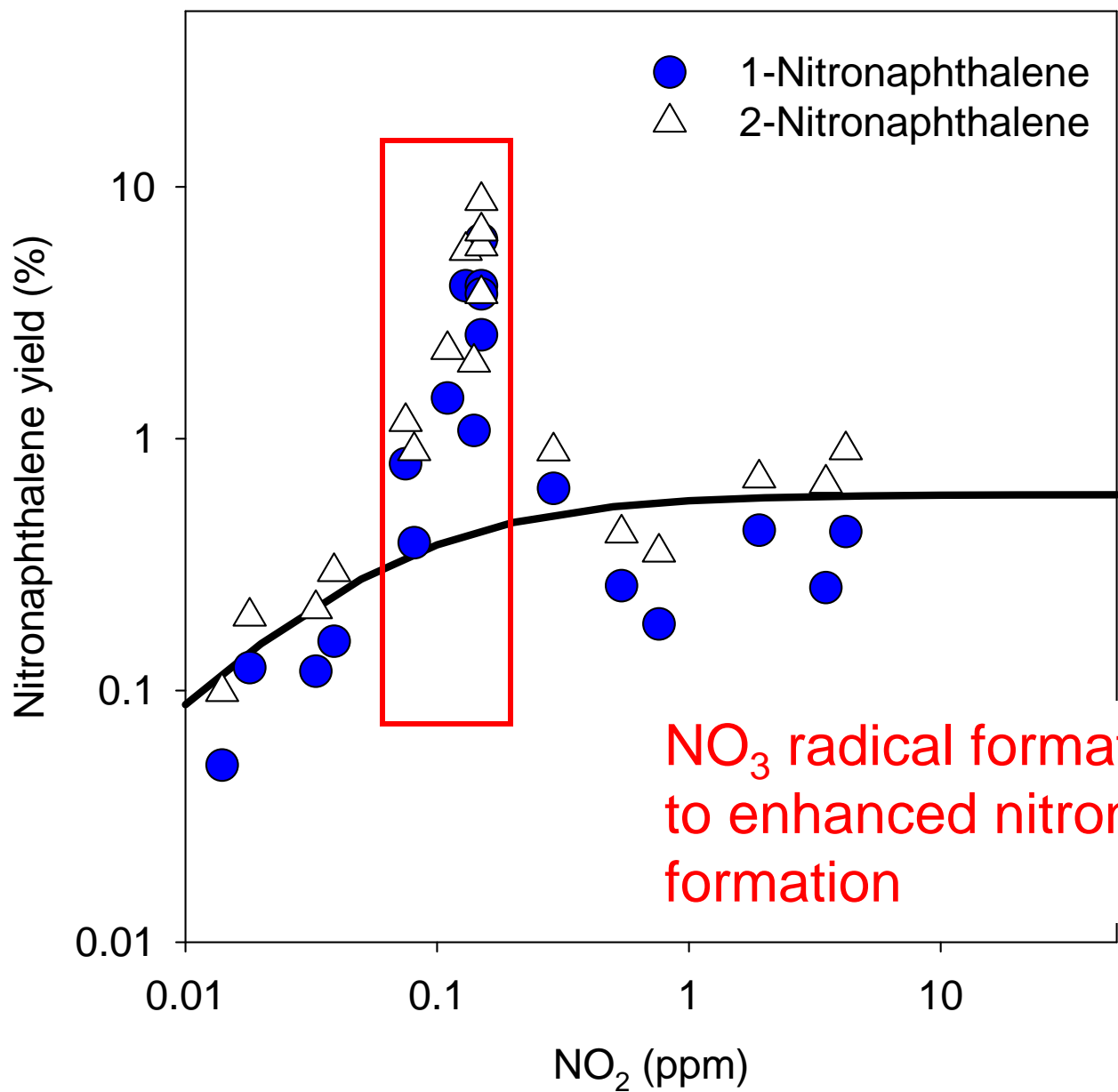
Analysis methods

- Toluene and naphthalene analyzed by GC-FID after collection of gas samples onto Tenax-TA solid adsorbent.
- Naphthalene and biphenyl analyzed by GC-FID after exposure of PDMS SPME fiber to chamber contents.
- Nitroaromatics analyzed by GC/MS-NCI after exposure of PDMS/DVB SPME fiber to chamber contents.

3-Nitrotoluene formation from OH + toluene



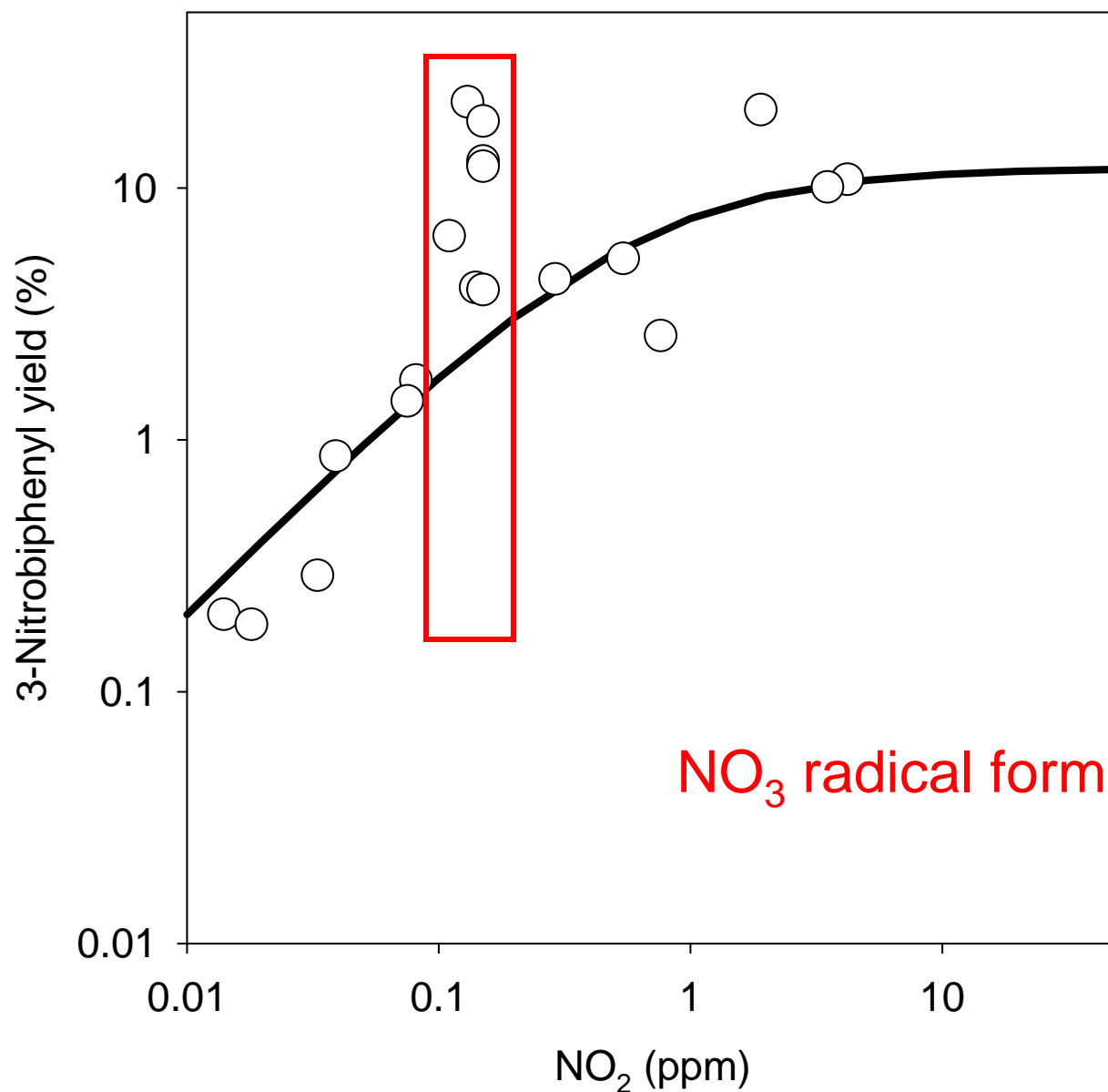
1- and 2-Nitronaphthalene formation from OH + naphthalene



Adduct + O₂ and NO₂ reactions equal at 60 ppb NO₂. $\alpha = 0.6\%$.

NO₃ radical formation likely, leading to enhanced nitronaphthalene formation

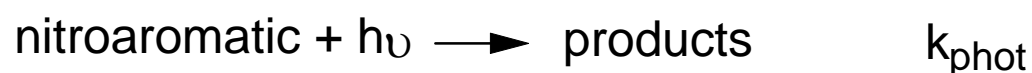
3-Nitrobiphenyl formation from OH + biphenyl



Adduct reactions with O₂ and NO₂ equal at 600 ppb NO₂. $\alpha = 12\%$.

NO₃ radical formation likely

Aromatic and nitroaromatic concentrations were measured at Upland, CA (1000-1500 hr, October 2006)



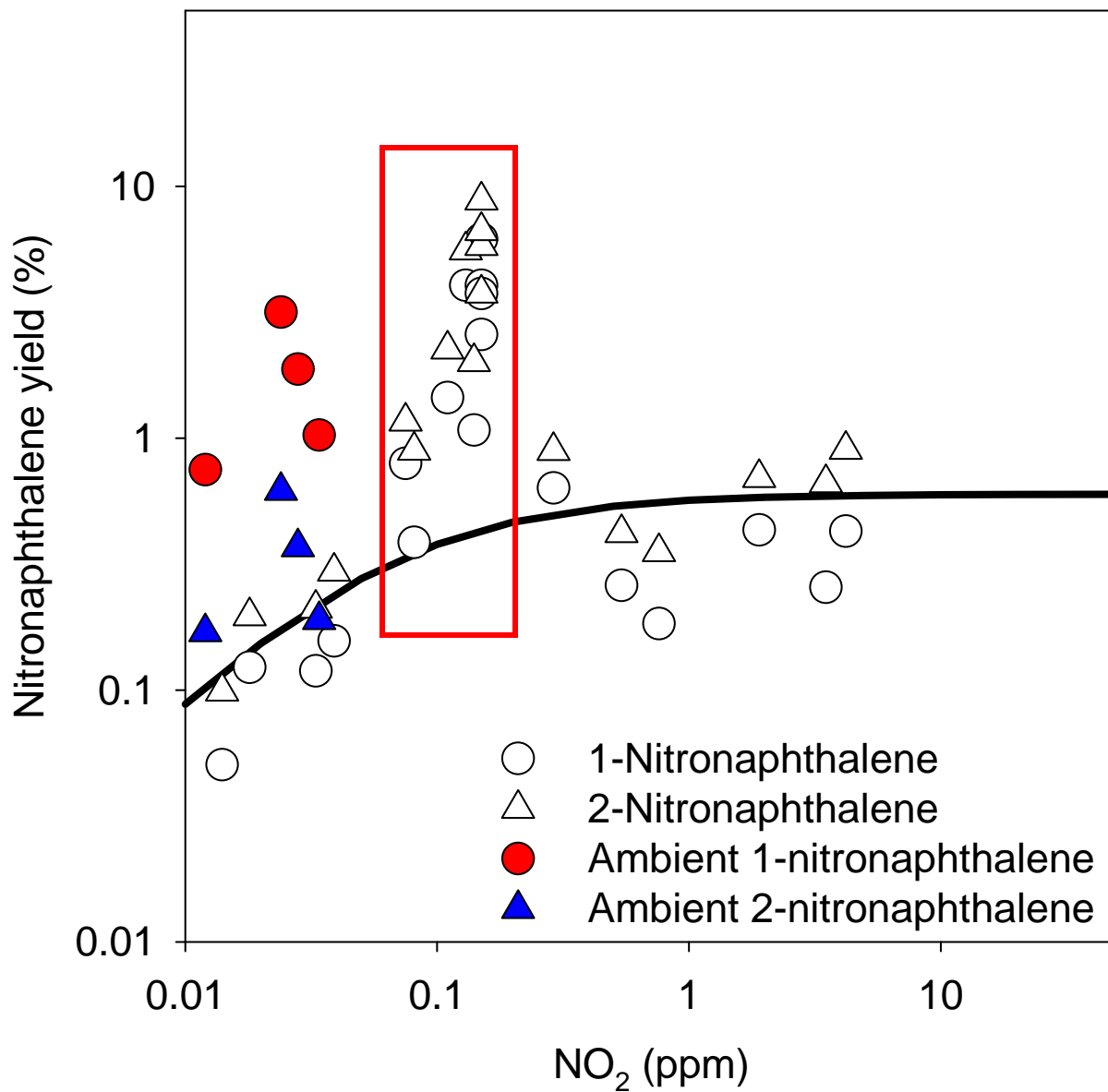
No photolysis of 3-nitrobiphenyl or 3-nitrotoluene assumed

$$\frac{[\text{nitroaromatic}]}{[\text{aromatic}]} = \frac{\alpha k_{OH}[\text{OH}]}{k_d + k_{phot}}$$

$$\left(\frac{[\text{nitroaromatic}]}{[\text{aromatic}]} \right) \Big/ \left(\frac{[\text{3-nitrotoluene}]}{[\text{toluene}]} \right) = \left(\frac{\alpha k_{OH}}{k_d + k_{phot}} \right)^{\text{aromatic}} \Big/ \left(\frac{\alpha k_{OH}}{k_d + k_{phot}} \right)^{\text{toluene}}$$

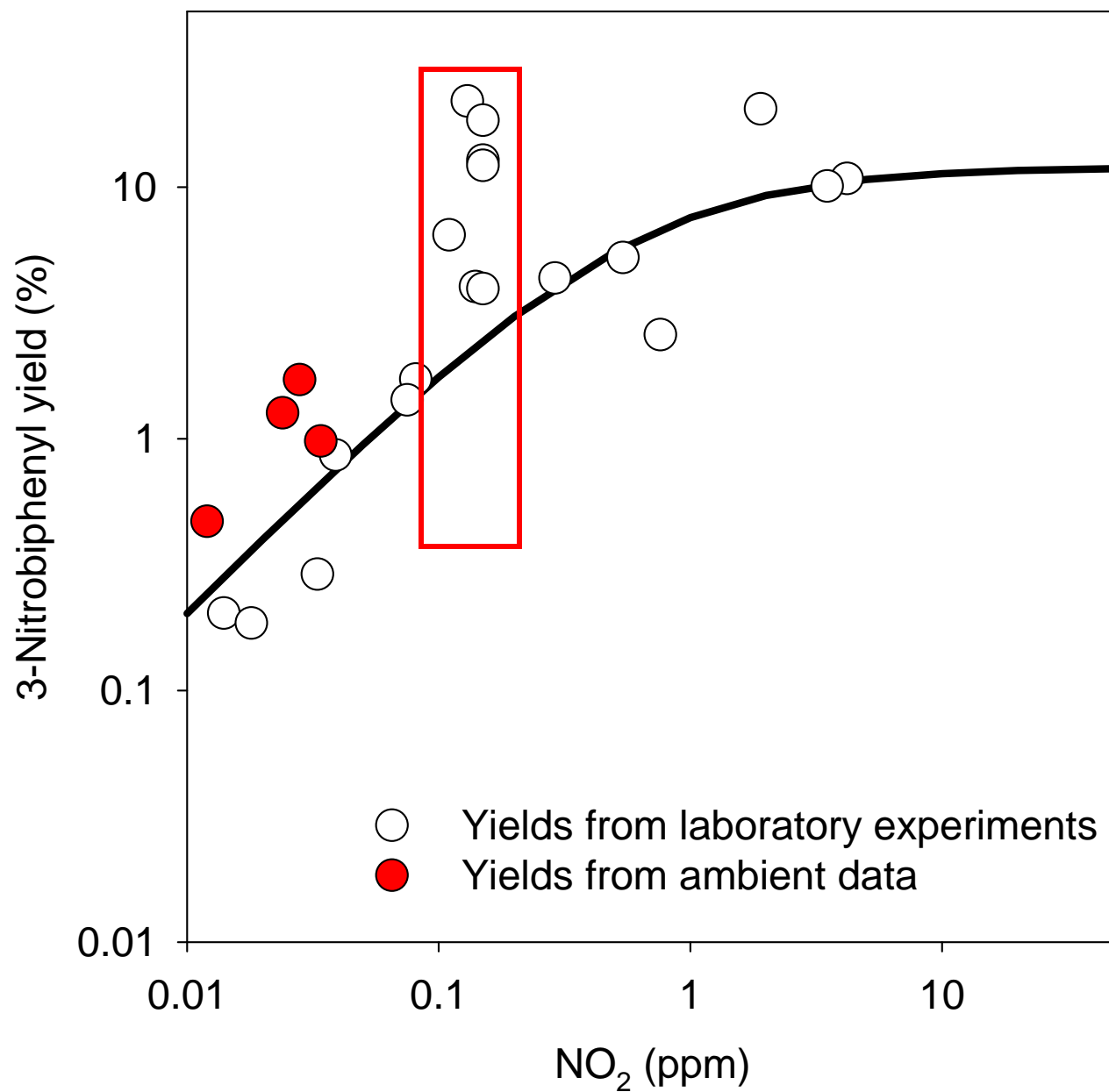
Get from our laboratory data for the ambient NO_2 concentration

1- and 2-Nitronaphthalene formation from OH + naphthalene



1-Nitronaphthalene?

3-Nitrobiphenyl formation from OH + biphenyl



Nitroaromatic formation from OH reactions

- The dependence of the 3-nitrotoluene formation yields from OH + toluene on NO₂ is totally consistent with literature kinetic and mechanistic data. The OH-toluene adducts react with O₂ under atmospheric conditions.
- The OH-biphenyl adducts react dominantly with NO₂ down to ~600 ppb of NO₂, and the OH-naphthalene adducts react dominantly with NO₂ down to ~60 ppb of NO₂.
- Laboratory data are generally consistent with ambient measurements of aromatics and their nitro-products.



Acknowledgements:

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undergraduate)

Dr. Sulekha Chattopadhyay
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now at ARB)