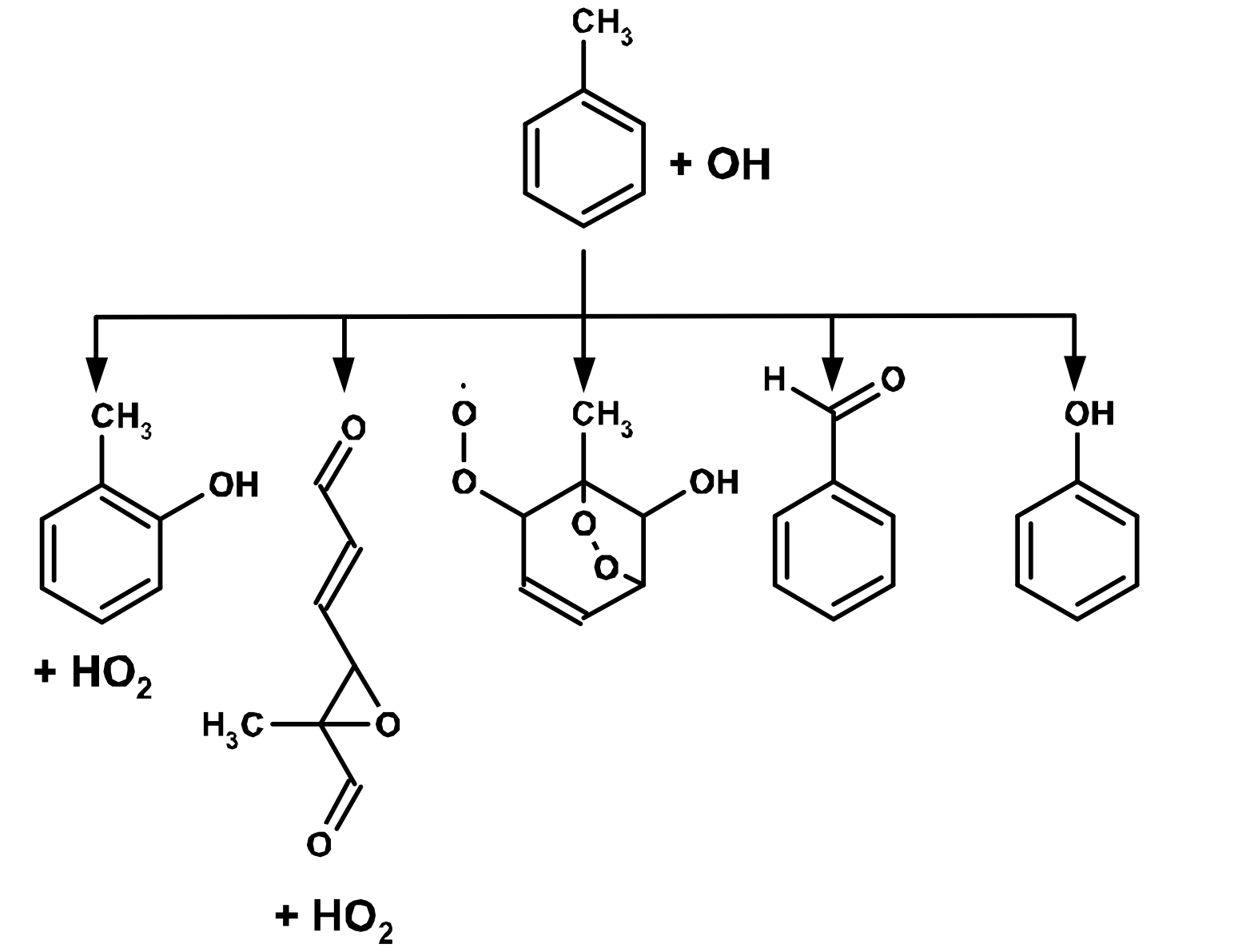
JÜLICH
FORSCHUNGSZENTRUM

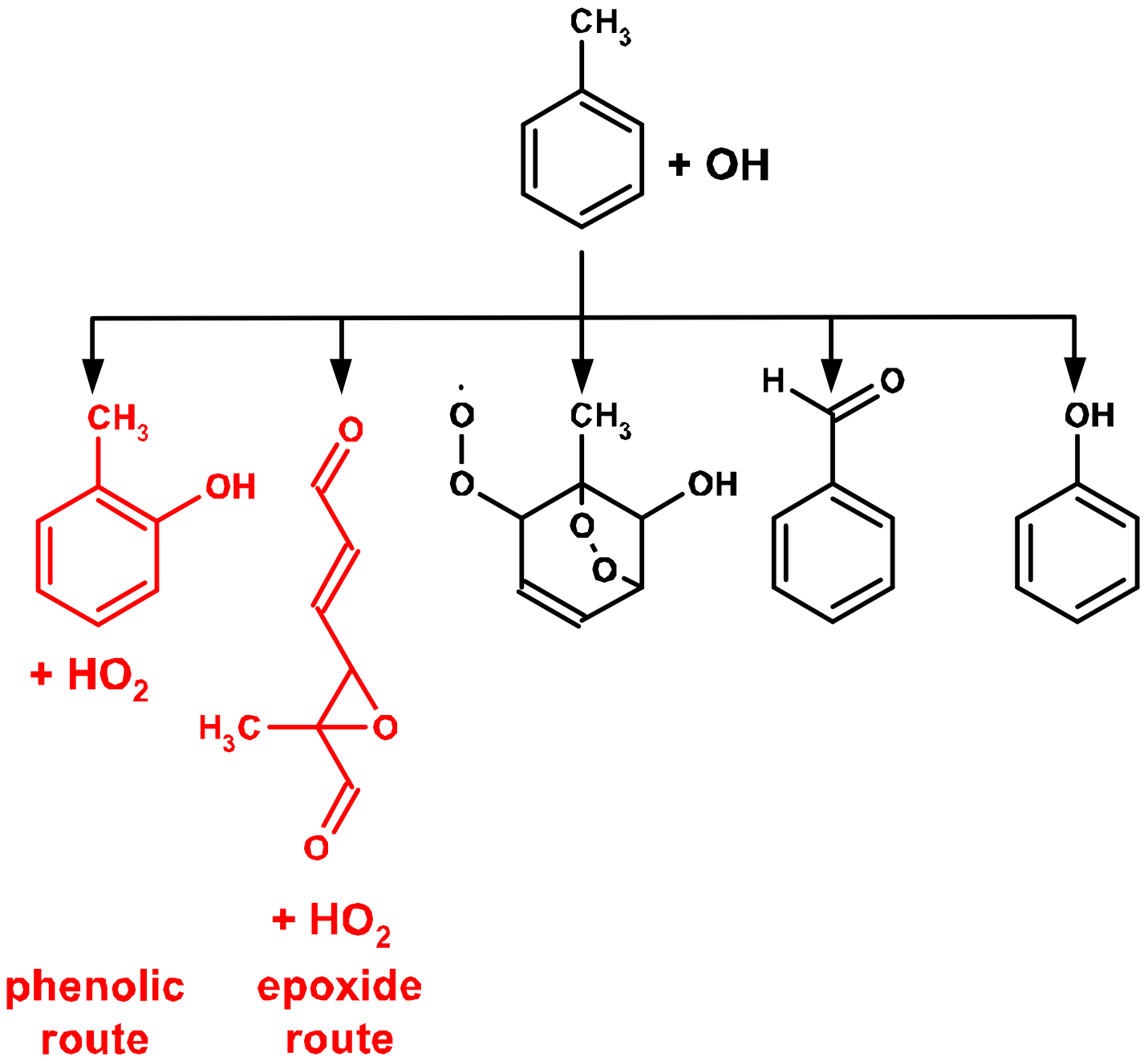
Secondary HO_2 formation from the OH-initiated photo-oxidation of aromatic hydrocarbons under atmospheric conditions in the absence of NO

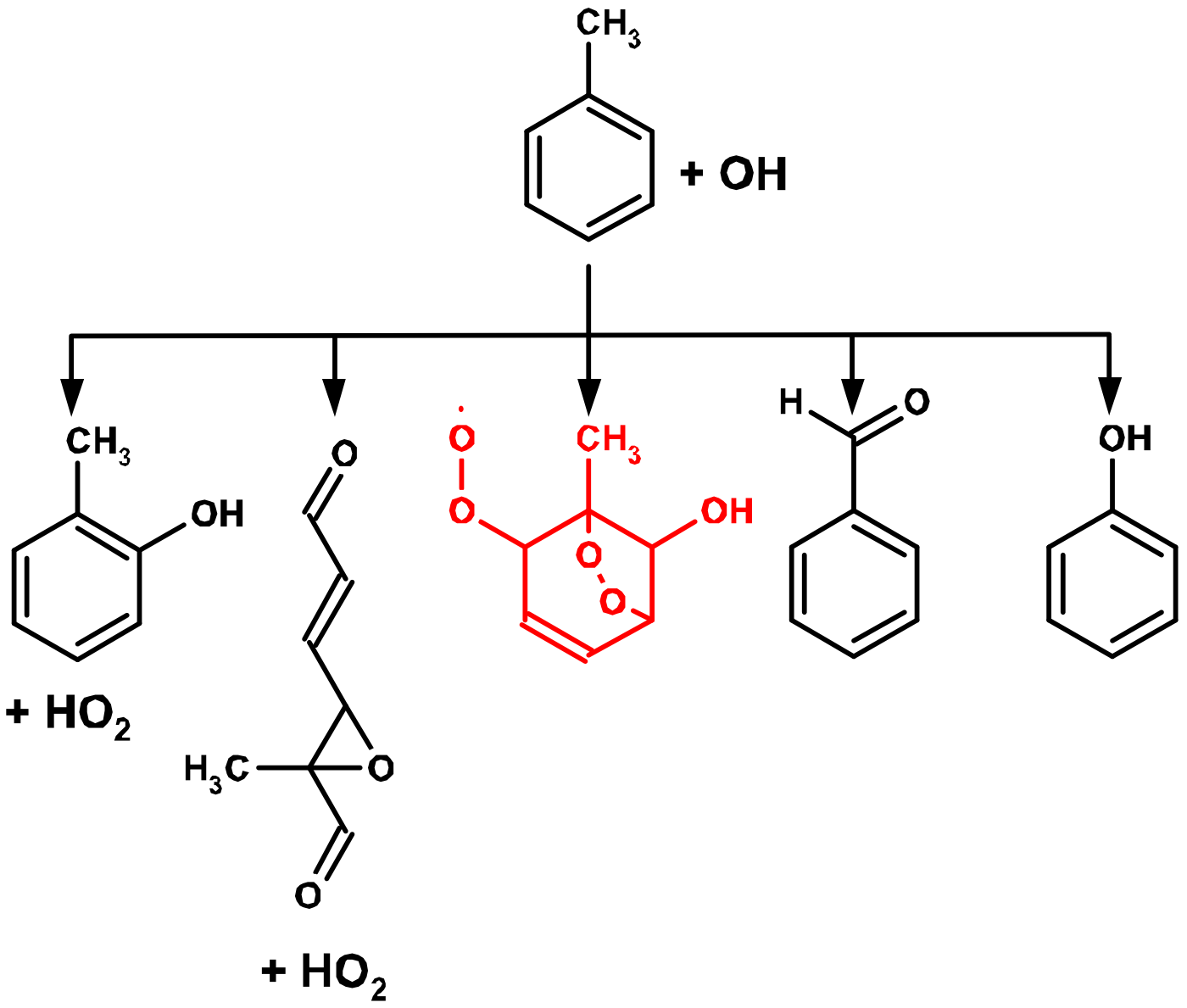
| Sascha Nehr, Birger Bohn, Hendrik Fuchs and Andreas Hofzumahaus

Secondary HO_2 formation

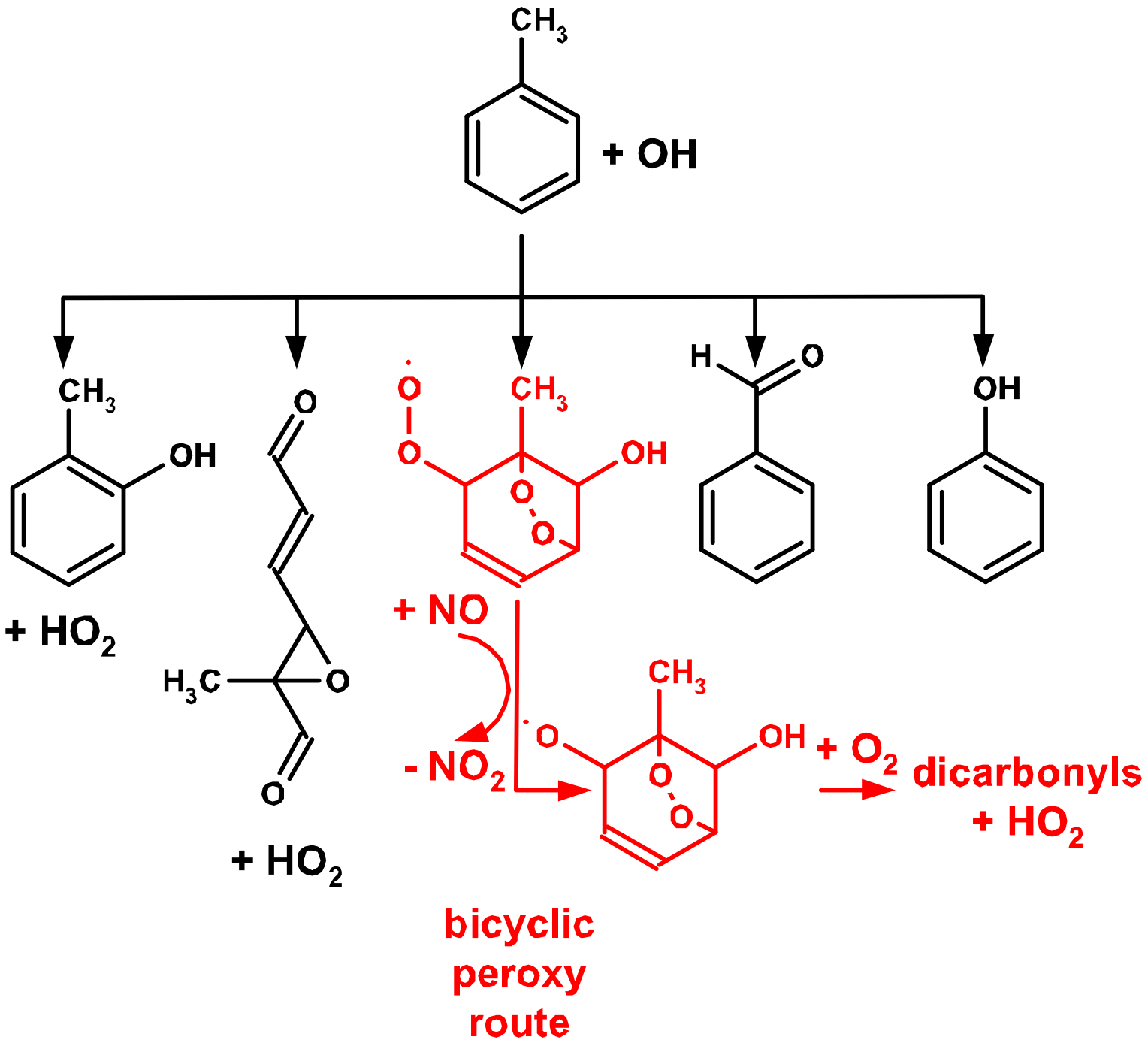
Delayed HO_2 formation	Prompt HO_2 formation
$CH_4 + OH \rightarrow CH_3 + H_2O$ $CH_3 + O_2 \rightarrow CH_3O_2$ $CH_3O_2 + NO \rightarrow CH_3O + NO_2$ $CH_3O + O_2 \rightarrow HCHO + \mathbf{HO_2}$	$CO + OH \rightarrow CO_2 + H$ $H + O_2 \rightarrow \mathbf{HO_2}$ ➔No preceding RO_2+NO reaction other examples: HCHO, H_2, C_2H_2

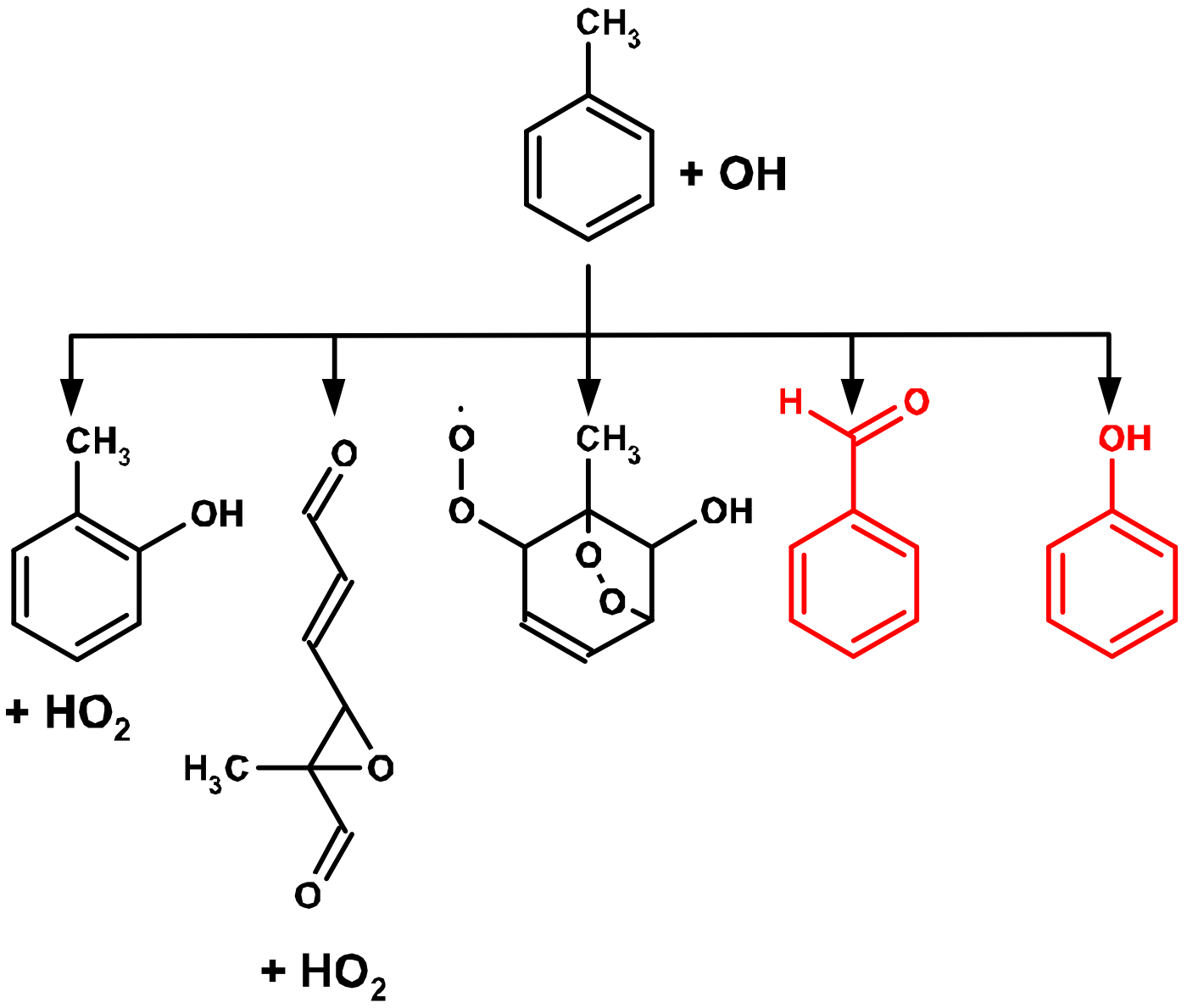

CH3
+ OH
CH3
OH
+ HO2
O
H3C
O
O
+ HO2
O
O
CH3
OH
O
O
H
O
OH
phenolic route
epoxide route
bicyclic peroxy route
H-atom abstraction
dealkylation

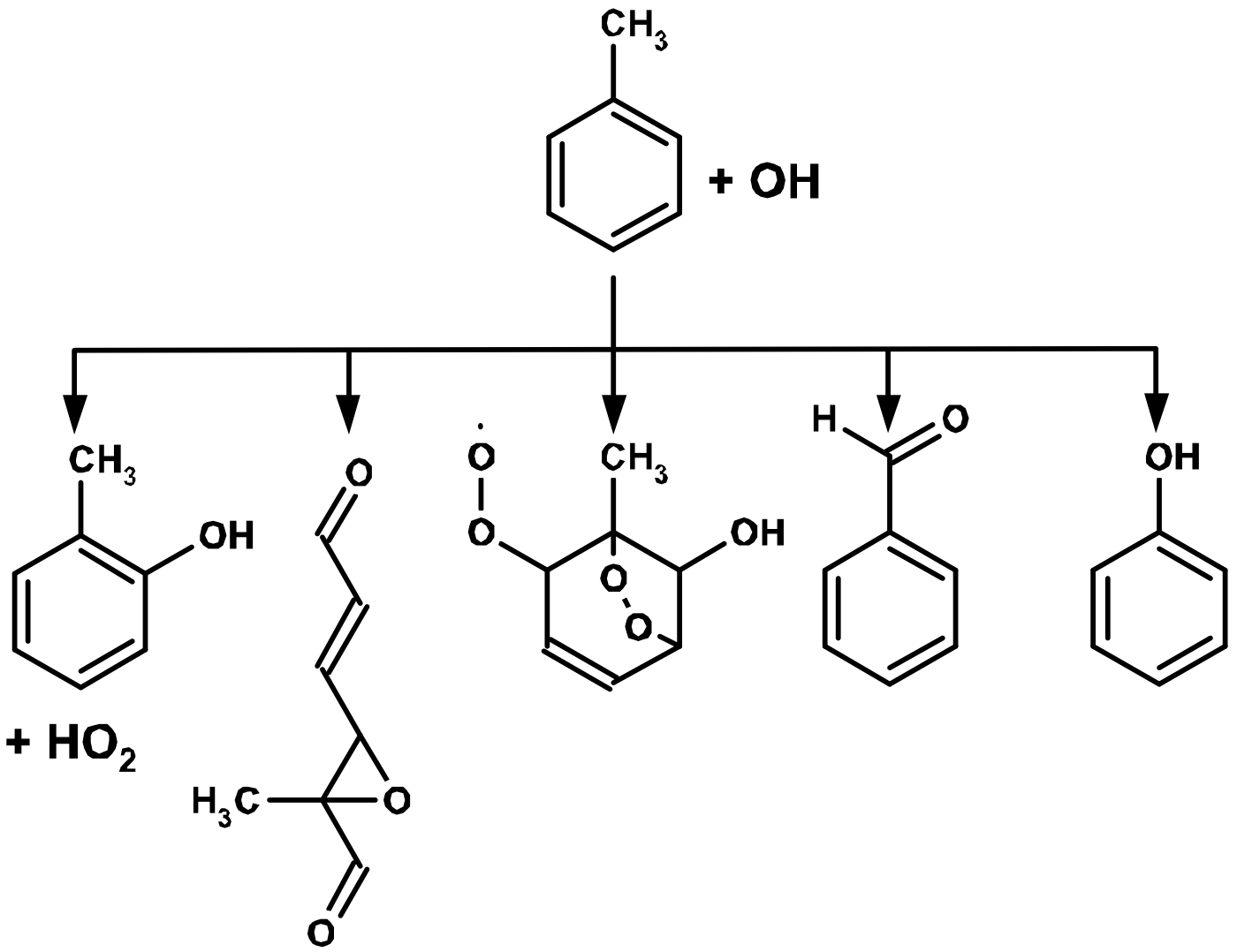

CH3
+ OH
CH3
OH
+ HO2
O
H3C
O
O
+ HO2
O
O
CH3
OH
O
O
H
O
OH
phenolic route
epoxide route



bicyclic peroxy route


CH3
+ OH
CH3
OH
+ HO2
O
O
H3C
O
O
+ HO2
O
O
CH3
OH
O
O
+ NO
- NO2
CH3
O
OH
O
O
+ O2
dicarbonyls
+ HO2
bicyclic
peroxy
route


CH3
+ OH
CH3
OH
+ HO2
O
H3C
O
O
+ HO2
O
O
CH3
OH
O
O
H
O
OH
H-atom abstraction
dealkylation



MCM v3.2				Noda et al. 2009
18%	10%	65%	7%	5%

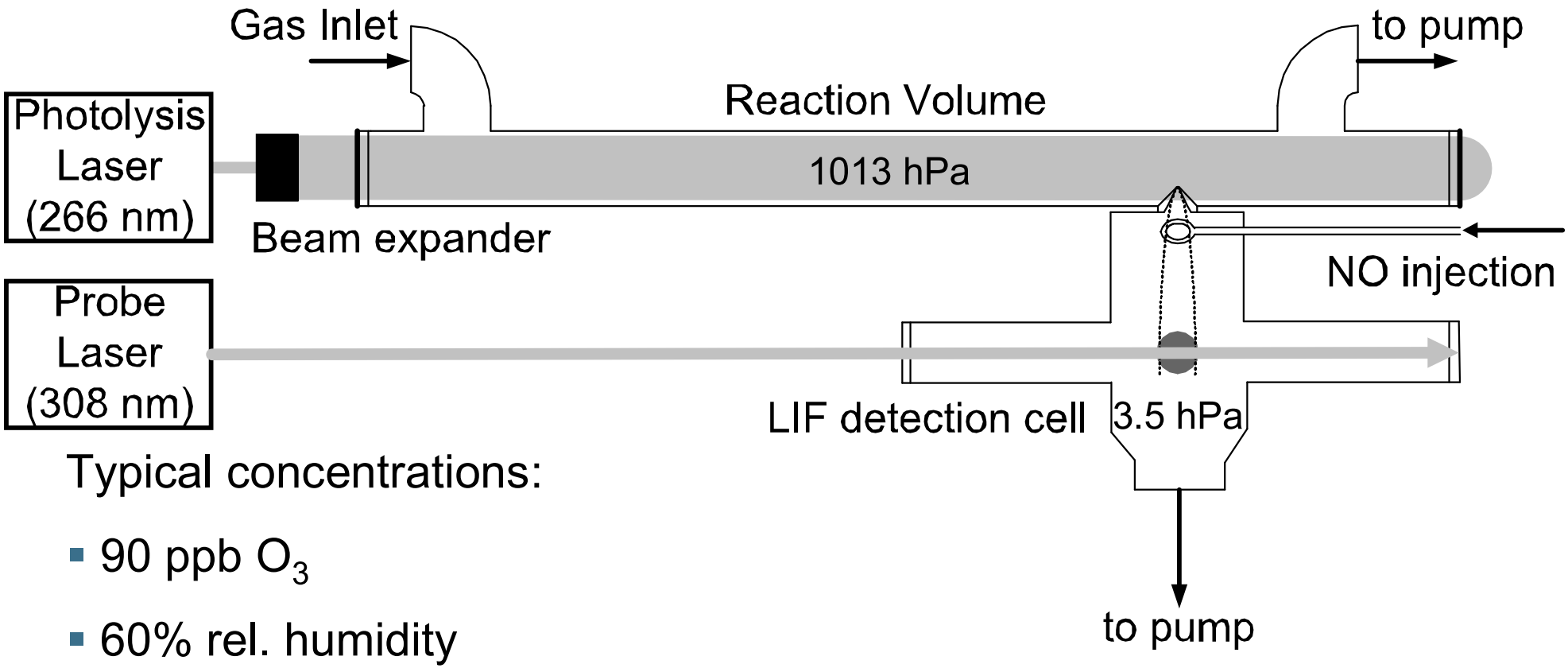
Objectives of this study

- Measurement of prompt HO_2 yields Φ_{HO2} from aromatics
- Comparison of Φ_{HO2} to other product yields from literature

➔ Does Φ_{HO2} match the sum of ($\Phi_{Phenolic}$ + $\Phi_{Epoxide}$)?

➔ Does (1-Φ_{HO2}) match the sum of ($\Phi_{Dicarbonyl}$ + $\Phi_{Benzaldehyde}$ + $\Phi_{Dealkylation}$)?

Experimental Setup



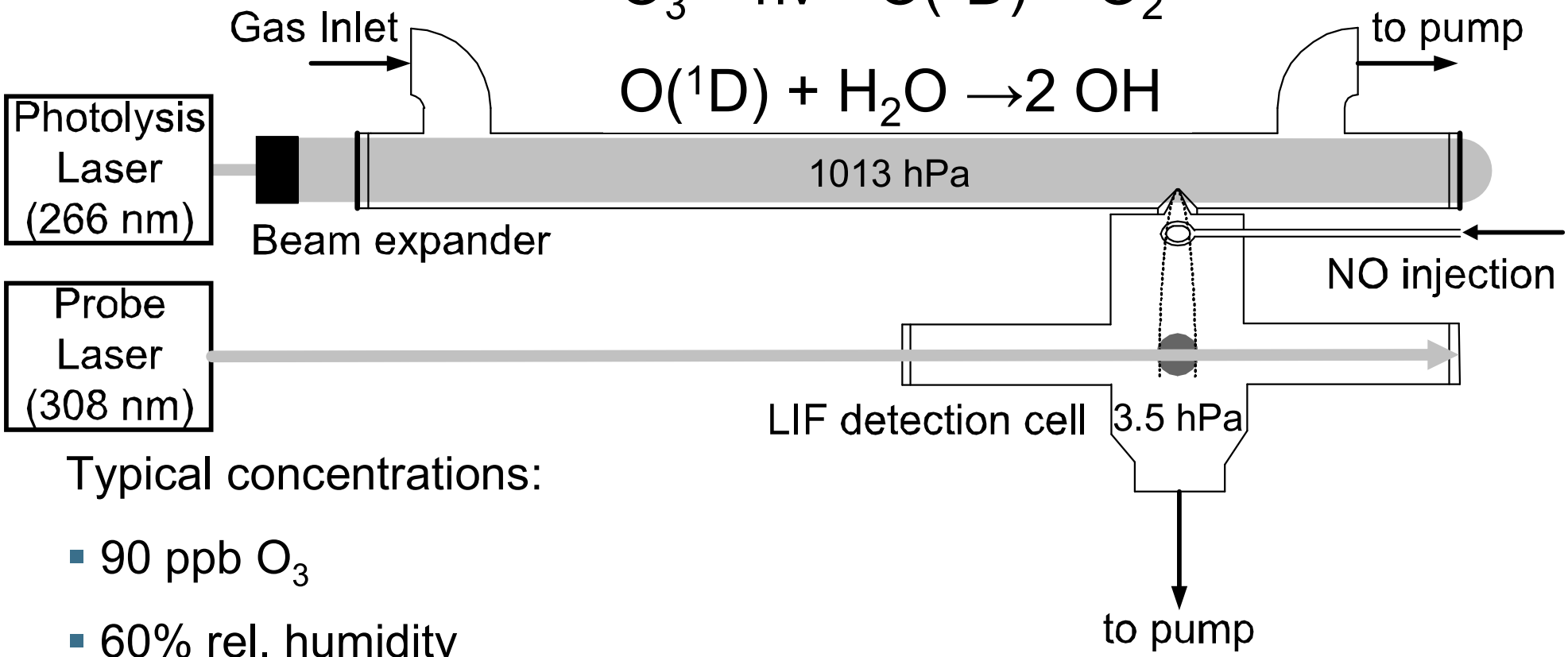
Typical concentrations:

- 90 ppb O_3
- 60% rel. humidity
- 200 ppb toluene
- $[OH]_0$: $5 \times 10^9 cm^{-3}$

Experimental Setup

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

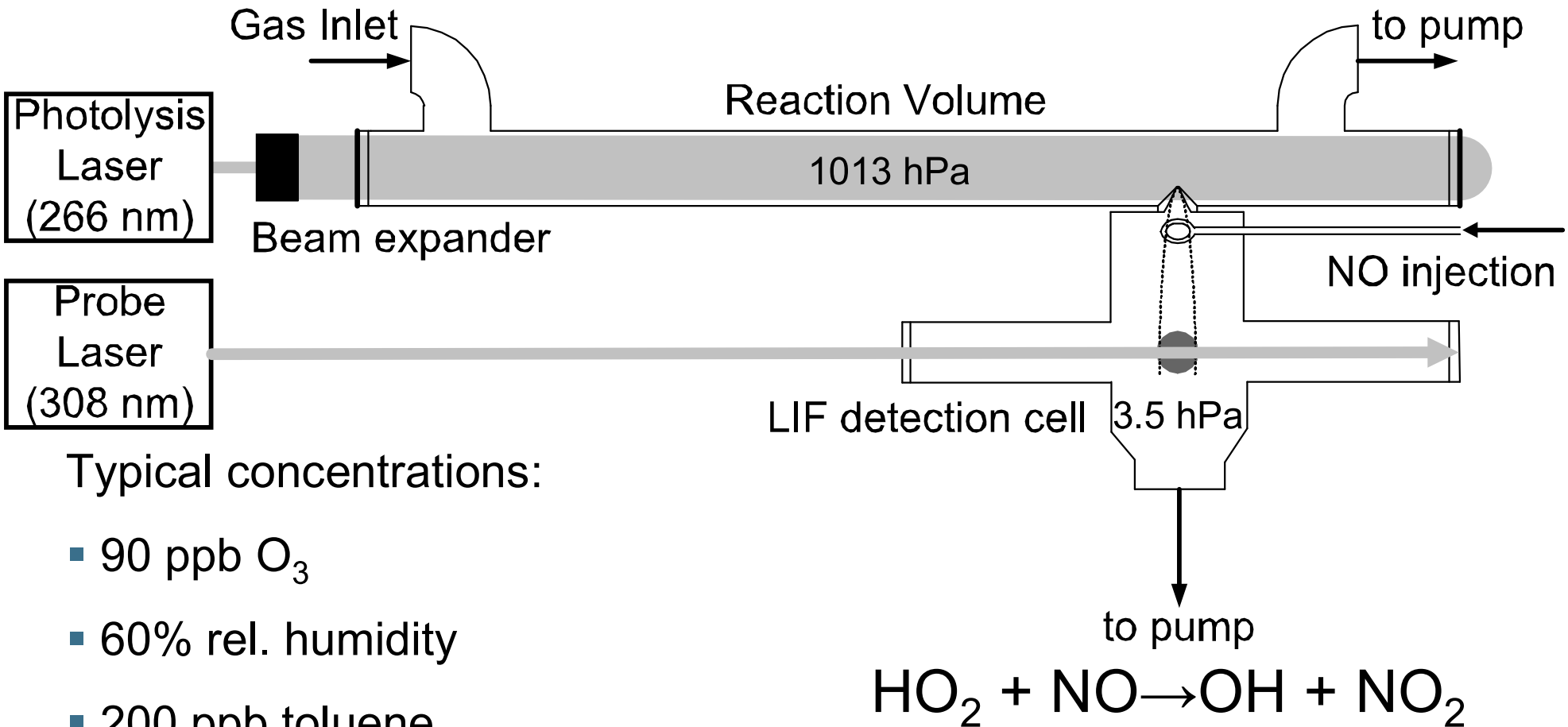
$$O(^1D) + H_2O \rightarrow 2\ OH$$



Typical concentrations:

- 90 ppb O_3
- 60% rel. humidity
- 200 ppb toluene
- $[OH]_0$: $5 \times 10^9 cm^{-3}$

Experimental Setup

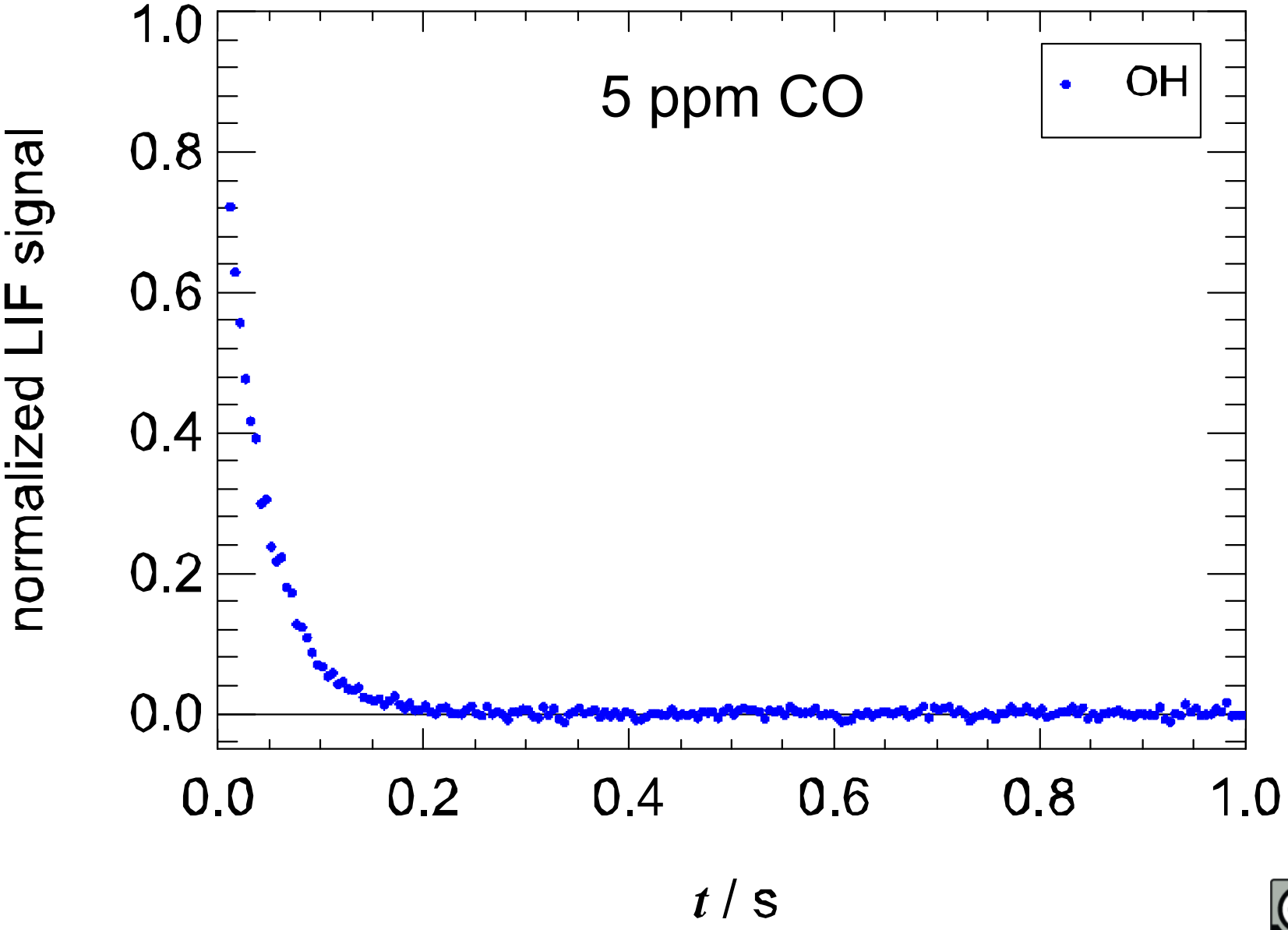


Typical concentrations:

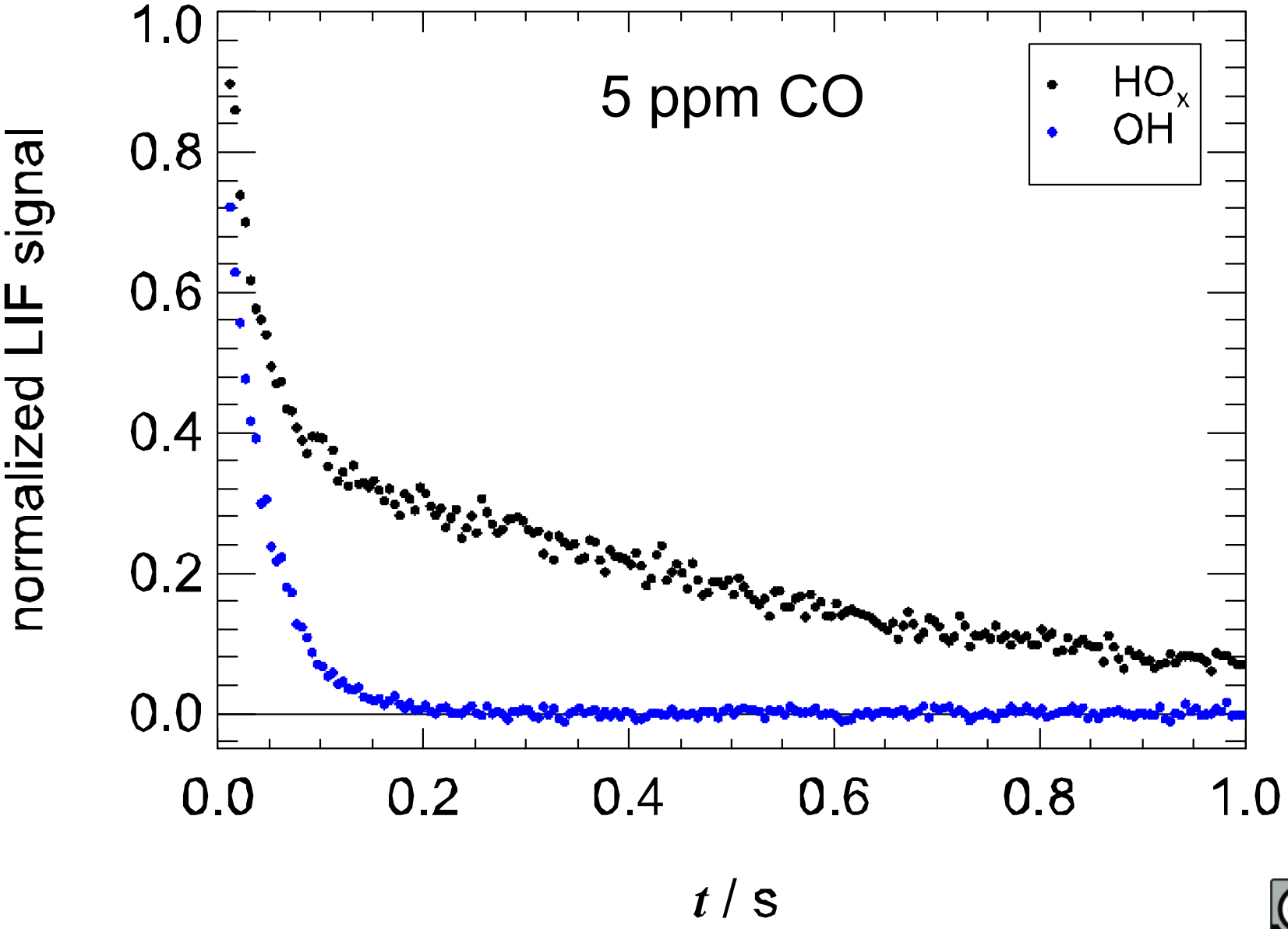
- 90 ppb O_3
- 60% rel. humidity
- 200 ppb toluene
- $[OH]_0$: $5x10^9 cm^{-3}$

$$HO_2 + NO \rightarrow OH + NO_2$$

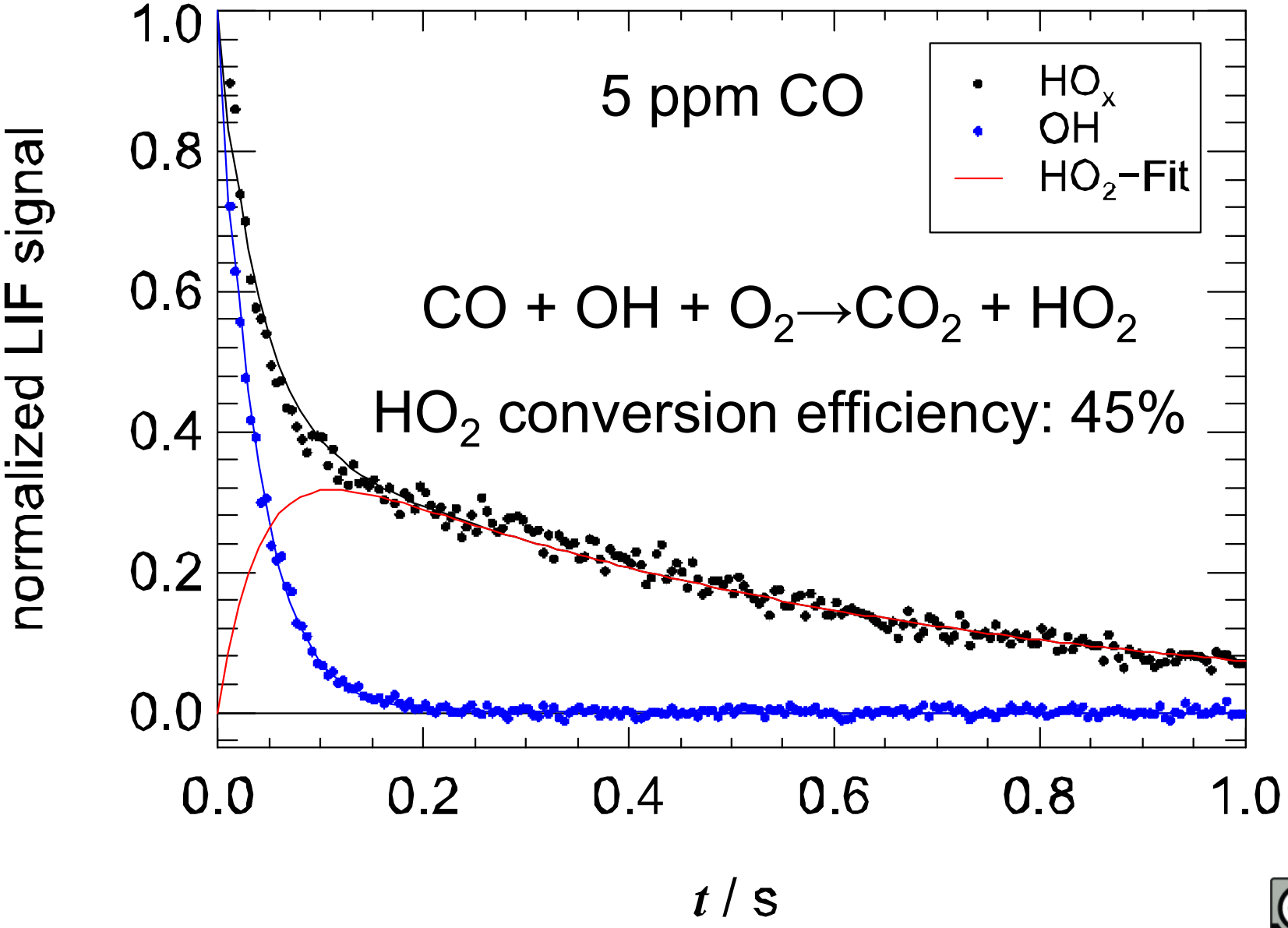
OH + CO

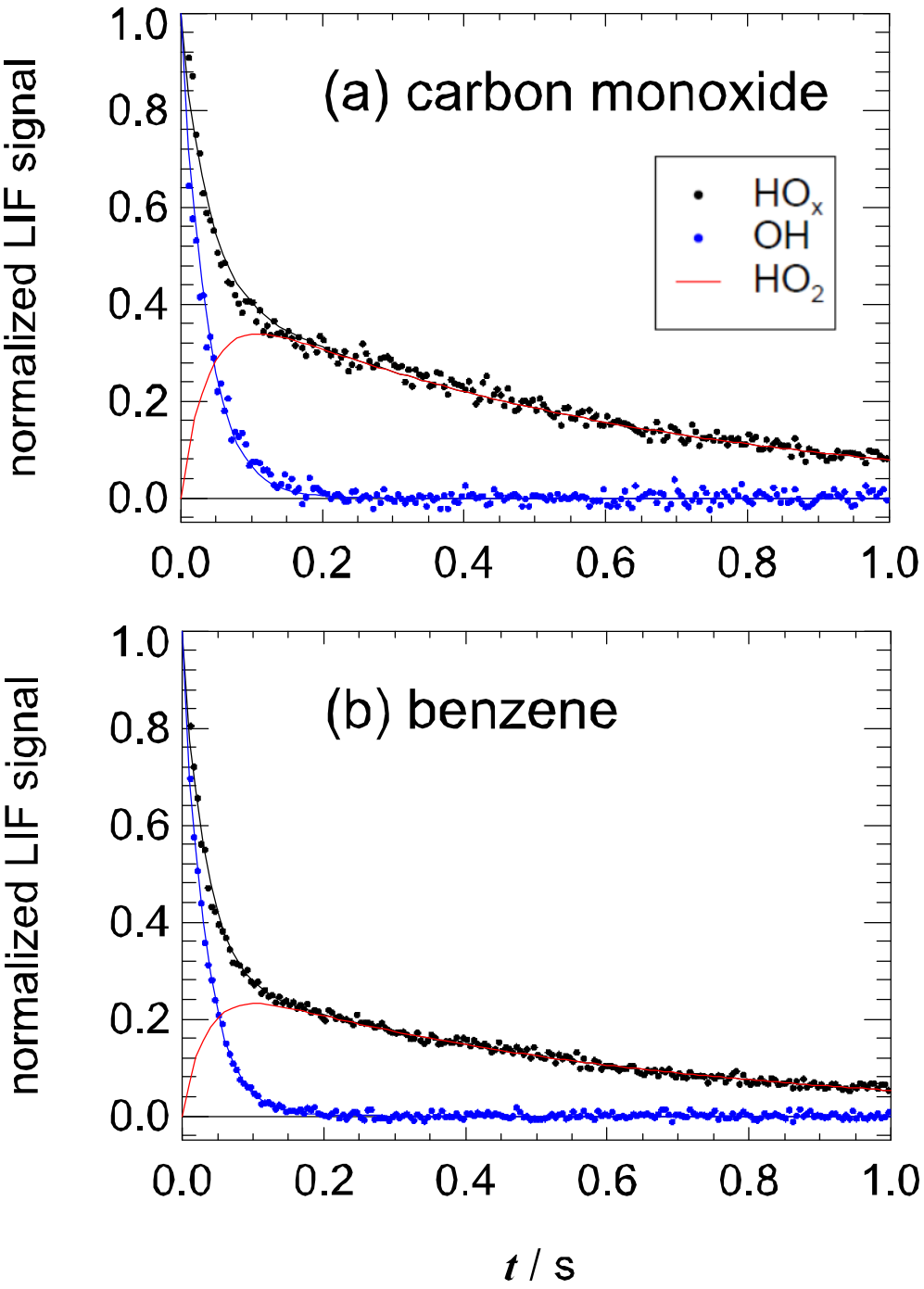

5 ppm CO
OH
normalized LIF signal
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
t / s

OH + CO



OH + CO





OH + benzene

- Curve-fitting of analytical solutions
- Φ_{HO2}=0.69±0.10 obtained for benzene

Aromatic compound	$\Phi_{Phenolic}$ (MCM)	$\Phi_{Epoxide}$ (MCM)	$\Phi_{Dicarbonyl}$ (MCM)	$\Phi_{Benzaldehyde}$ (MCM)	Φ_{HO2} (this study)
benzene	0.53	0.12	0.35	-	0.69±0.10
toluene	0.18	0.10	0.65	0.07	0.42±0.11
ethylbenzene	0.18	0.10	0.65	0.07	0.53±0.10
o-xylene	0.16	0.24	0.55	0.05	0.41±0.08
m-xylene	0.17	0.29	0.50	0.04	0.27±0.06
p-xylene	0.12	0.16	0.62	0.10	0.40±0.09
1,2,3-trimethyl-benzene	0.03	0.21	0.70	0.06	0.31±0.06
1,2,4-trimethyl-benzene	0.03	0.30	0.61	0.06	0.37±0.09
1,3,5-trimethyl-benzene	0.04	0.14	0.79	0.03	0.29±0.08

Aromatic compound	$\Phi_{Phenolic}$ (MCM)	$\Phi_{Epoxide}$ (MCM)	$\Phi_{Dicarbonyl}$ (MCM)	$\Phi_{Benzaldehyde}$ (MCM)	Φ_{HO2} (this study)
benzene	0.53	0.12	0.35	-	0.69±0.10
toluene	0.18	0.10	0.65	0.07	0.42±0.11
ethylbenzene	0.18	0.10	0.65	0.07	0.53±0.10
o-xylene	0.16	0.24	0.55	0.05	0.41±0.08
m-xylene	0.17	0.29	0.50	0.04	0.27±0.06
p-xylene	0.12	0.16	0.62	0.10	0.40±0.09
1,2,3-trimethyl-benzene	0.03	0.21	0.70	0.06	0.31±0.06
1,2,4-trimethyl-benzene	0.03	0.30	0.61	0.06	0.37±0.09
1,3,5-trimethyl-benzene	0.04	0.14	0.79	0.03	0.29±0.08

Aromatic compound	$\Phi_{Phenolic}$ (MCM)	$\Phi_{Epoxide}$ (MCM)	$\Phi_{Dicarbonyl}$ (MCM)	$\Phi_{Benzaldehyde}$ (MCM)	Φ_{HO2} (this study)
benzene	0.53	0.12	0.35	-	0.69±0.10
toluene	0.18	0.10	0.65	0.07	0.42±0.11
ethylbenzene	0.18	0.10	0.65	0.07	0.53±0.10
o-xylene	0.16	0.24	0.55	0.05	0.41±0.08
m-xylene	0.17	0.29	0.50	0.04	0.27±0.06
p-xylene	0.12	0.16	0.62	0.10	0.40±0.09
1,2,3-trimethyl-benzene	0.03	0.21	0.70	0.06	0.31±0.06
1,2,4-trimethyl-benzene	0.03	0.30	0.61	0.06	0.37±0.09
1,3,5-trimethyl-benzene	0.04	0.14	0.79	0.03	0.29±0.08

Aromatic compound	$\Phi_{Phenolic}$ (MCM)	$\Phi_{Epoxide}$ (MCM)	$\Phi_{Dicarbonyl}$ (MCM)	$\Phi_{Benzaldehyde}$ (MCM)	Φ_{HO2} (this study)
benzene	0.53	0.12	0.35	-	0.69±0.10
toluene	0.18	0.10	0.65	0.07	0.42±0.11
ethylbenzene	0.18	0.10	0.65	0.07	0.53±0.10
o-xylene	0.16	0.24	0.55	0.05	0.41±0.08
m-xylene	0.17	0.29	0.50	0.04	0.27±0.06
p-xylene	0.12	0.16	0.62	0.10	0.40±0.09
1,2,3-trimethyl-benzene	0.03	0.21	0.70	0.06	0.31±0.06
1,2,4-trimethyl-benzene	0.03	0.30	0.61	0.06	0.37±0.09
1,3,5-trimethyl-benzene	0.04	0.14	0.79	0.03	0.29±0.08

OH + benzene
Φ_{HO2}=0.69±0.10

- Φ_{HO2} similar to $\Phi_{Phenolic}$

0.51±0.04	(Noda et al., 2009)
0.61±0.07	(Berndt et al., 2006)
0.53±0.07	(Volkamer et al., 2002)

➔ Epoxide products not observed!

- (1- Φ_{HO2})≈0.3 consistent with $\Phi_{Dicarbonyl}$

0.29±0.10	(Berndt et al., 2006)
0.35±0.10	(Volkamer et al., 2001)

Aromatic compound	$\Phi_{Phenolic}$ (MCM)	$\Phi_{Epoxide}$ (MCM)	$\Phi_{Dicarbonyl}$ (MCM)	$\Phi_{Benzaldehyde}$ (MCM)	Φ_{HO2} (this study)
benzene	0.53	0.12	0.35	-	0.69±0.10
toluene	0.18	0.10	0.65	0.07	0.42±0.11
ethylbenzene	0.18	0.10	0.65	0.07	0.53±0.10
o-xylene	0.16	0.24	0.55	0.05	0.41±0.08
m-xylene	0.17	0.29	0.50	0.04	0.27±0.06
p-xylene	0.12	0.16	0.62	0.10	0.40±0.09
1,2,3-trimethyl-benzene	0.03	0.21	0.70	0.06	0.31±0.06
1,2,4-trimethyl-benzene	0.03	0.30	0.61	0.06	0.37±0.09
1,3,5-trimethyl-benzene	0.04	0.14	0.79	0.03	0.29±0.08

OH + toluene
Φ_{HO2}=0.42±0.11

- Φ_{HO2} consistent with recent product study:

  $(\Phi_{Phenolic} + \Phi_{Epoxide})$=0.35±0.06 (Baltaretu et al., 2009)

- Discrepancies for $(1- \Phi_{HO2})$≈0.6

  $(\Phi_{Benzaldehyde} + \Phi_{Dicarbonyl})$=0.35±0.10 (Baltaretu et al., 2009)

  ➔Missing reactions?

Summary

- First measurement of prompt HO_2 yields from aromatics
- Complementary method to previous product studies

➔ <u>Benzene:</u>

Φ_{HO2} similar to $\Phi_{Phenolic}$,
non-phenol pathway of minor importance

➔ <u>Toluene, xylenes, and trimethylbenzenes:</u>

Φ_{HO2} significantly greater than $\Phi_{Phenolic}$
non-phenol pathways important

Supplementary information

- Results for OH + benzene recently published:

  ➔ S. Nehr, B. Bohn, H. Fuchs, A. Hofzumahaus, A. Wahner, *Phys. Chem. Chem. Phys.*, **2011**, DOI: 10.1039/c1cp20334g

- Results for other investigated aromatics are not yet published!

- Contact:

  ➔ Institut für Energie- und Klimaforschung IEK-8: Troposphäre, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
  E-mail: s.nehr@fz-juelich.de