Investigation of the VOC Degradation on Photocatalytic Paint Surfaces: Kinetic and Product Studies

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Motivation

- **Volatile organic components (VOC´s) important class of compounds for the atmosphere**

  - Formation of tropospheric ozone (smog)

  - VOCs in part, directly harmful:
    e.g. benzene carcinogenic

  - Formation of hazardous degradation products:
    Peroxyacylnitrates (PANs) and
    Aldehydes (e.g. formaldehyde)

  - Formation of secondary organic aerosols (SOA)

Aim of this Study

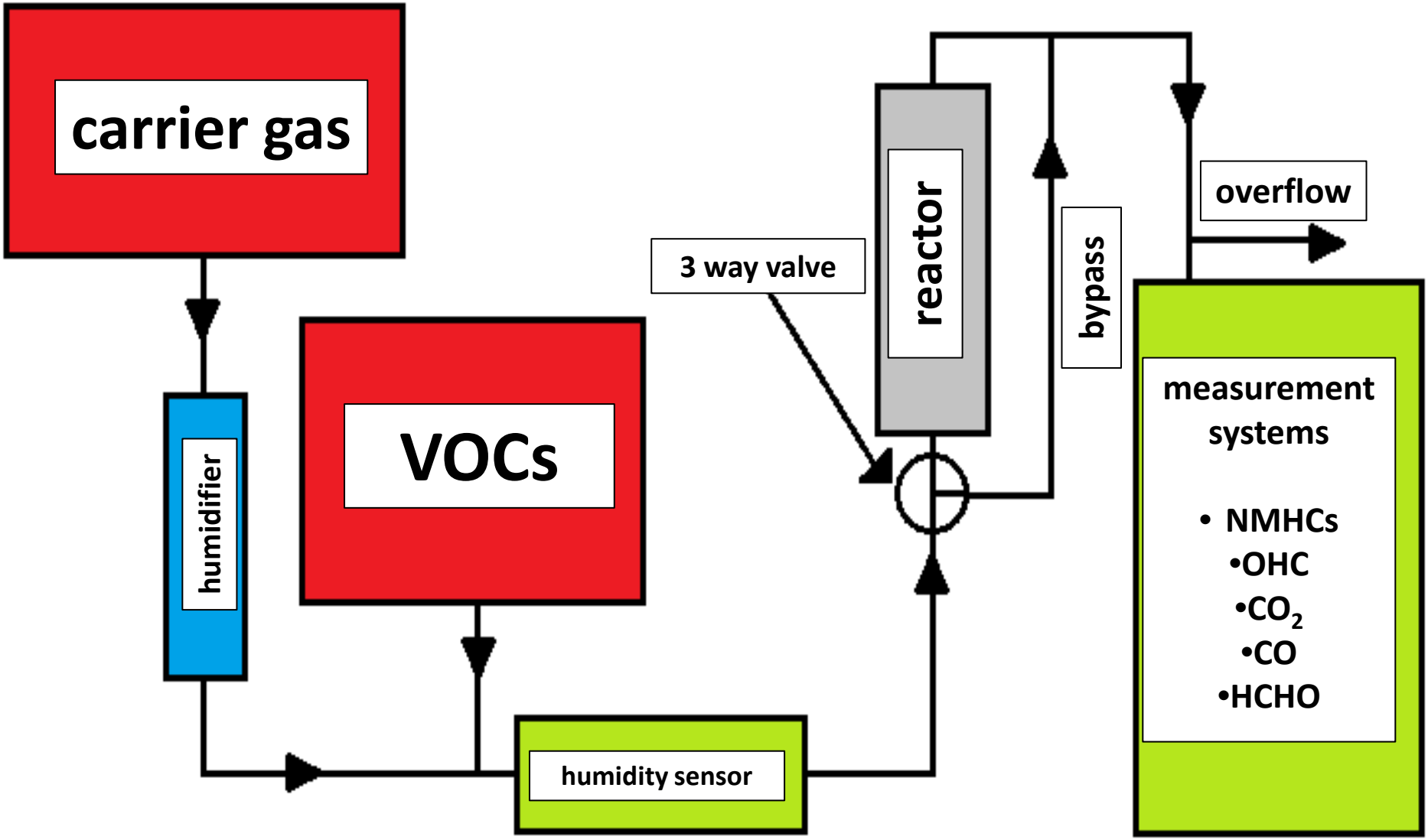
- Laboratory studies on the photocatalytic conversion of VOCs on TiO_2-doped wall paints:
  - benzene
  - toluene
  - iso-pentane
  - 1-butene

  → Important urban VOCs

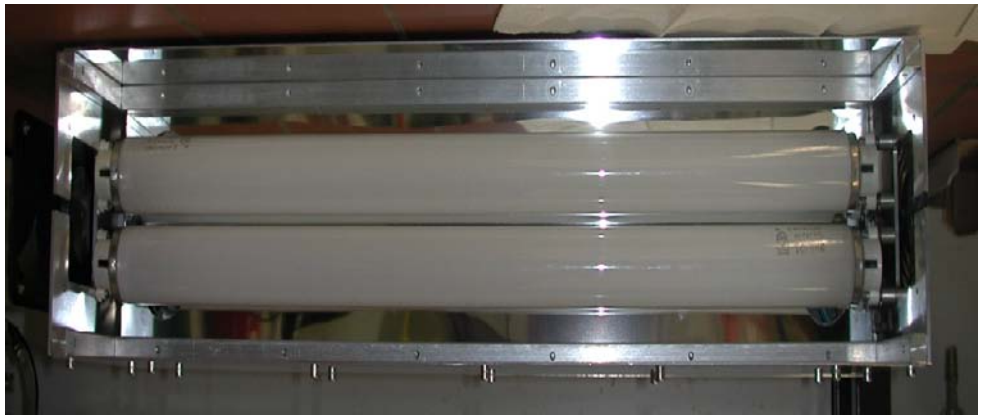
  under real atmospheric conditions

- ➢ kinetic parameters
- ➢ degradation products

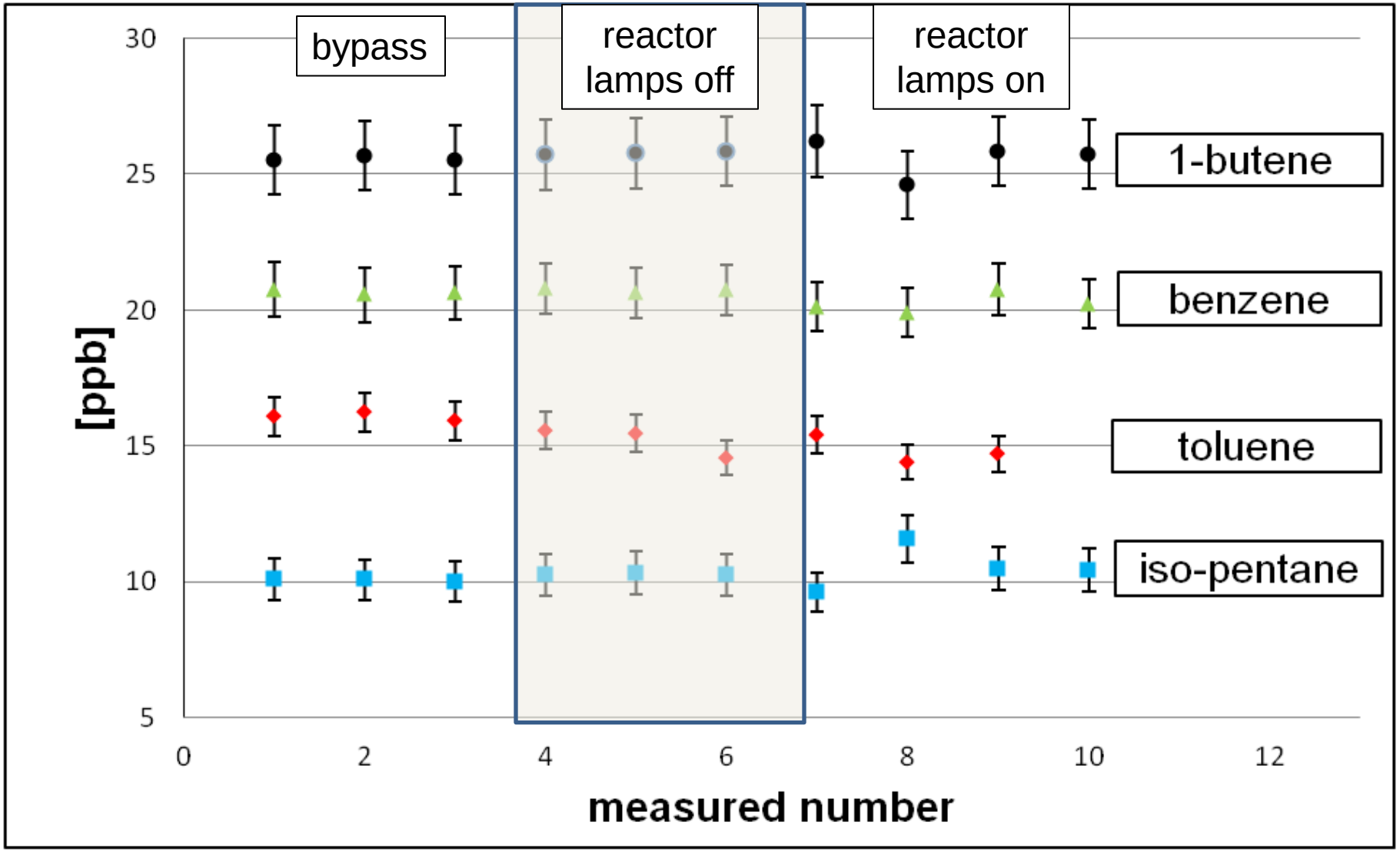
Experimental



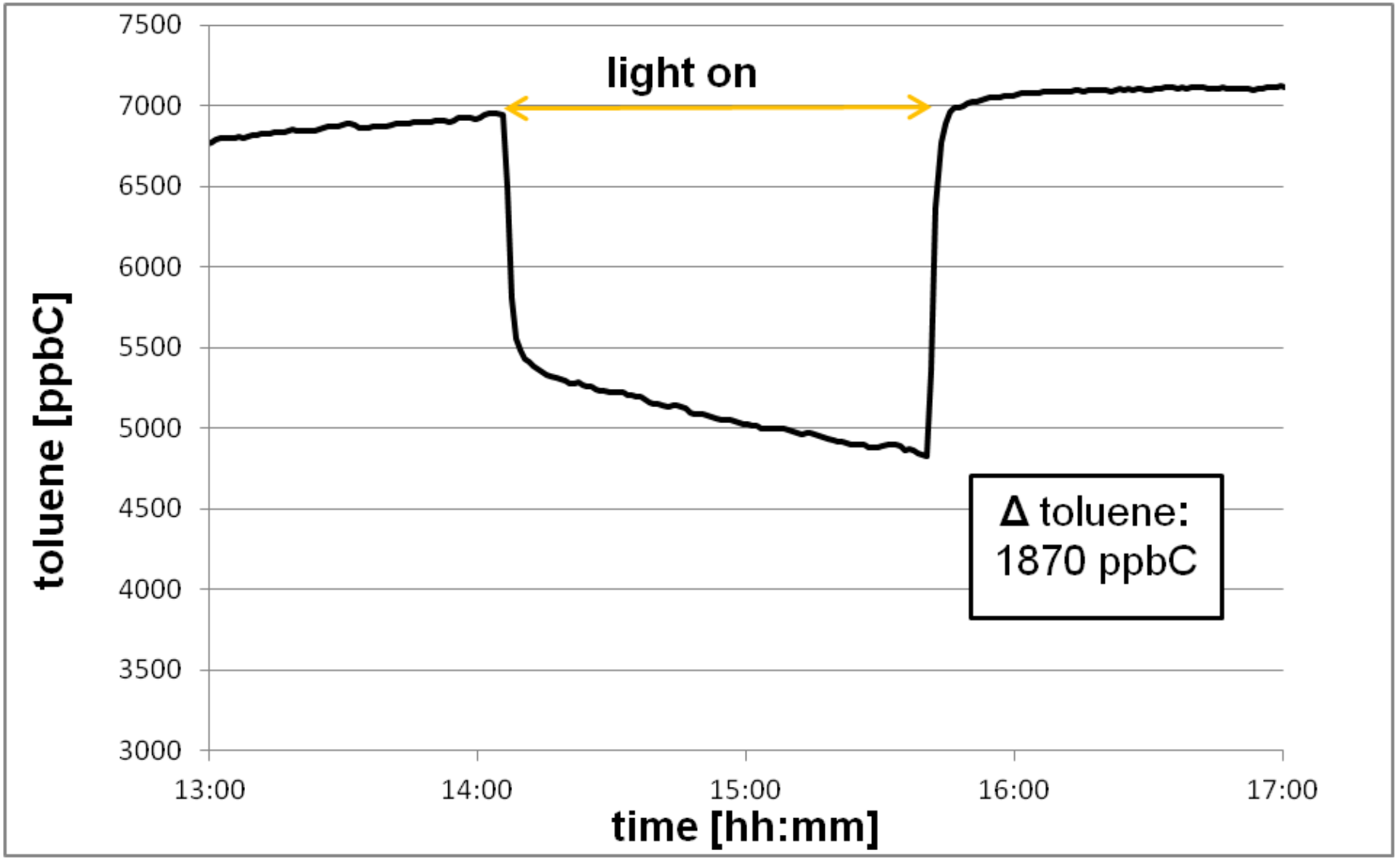
Reactors



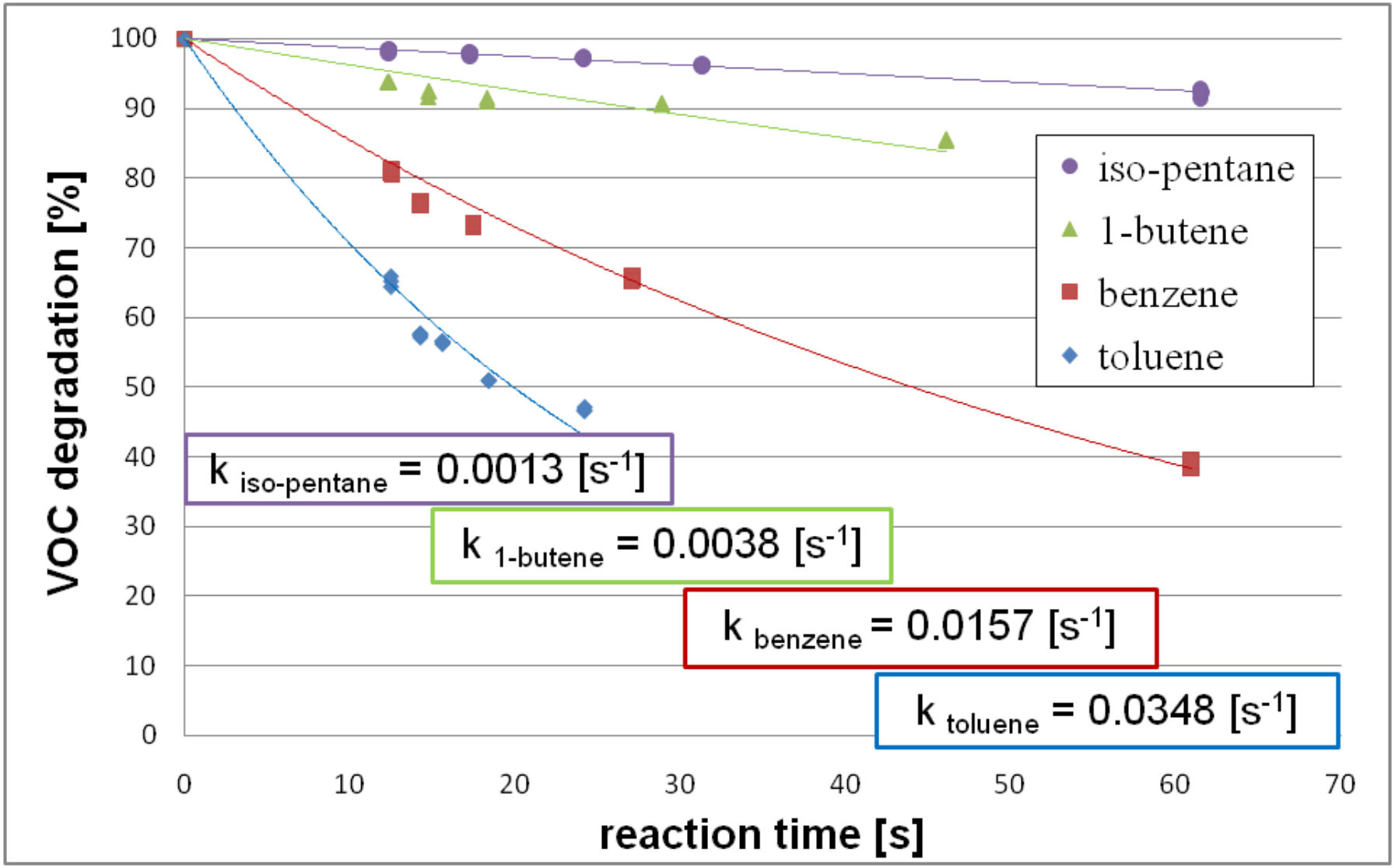
Blank Experiments without Paint



Experiment with Paint: Toluene



Reaction Kinetics



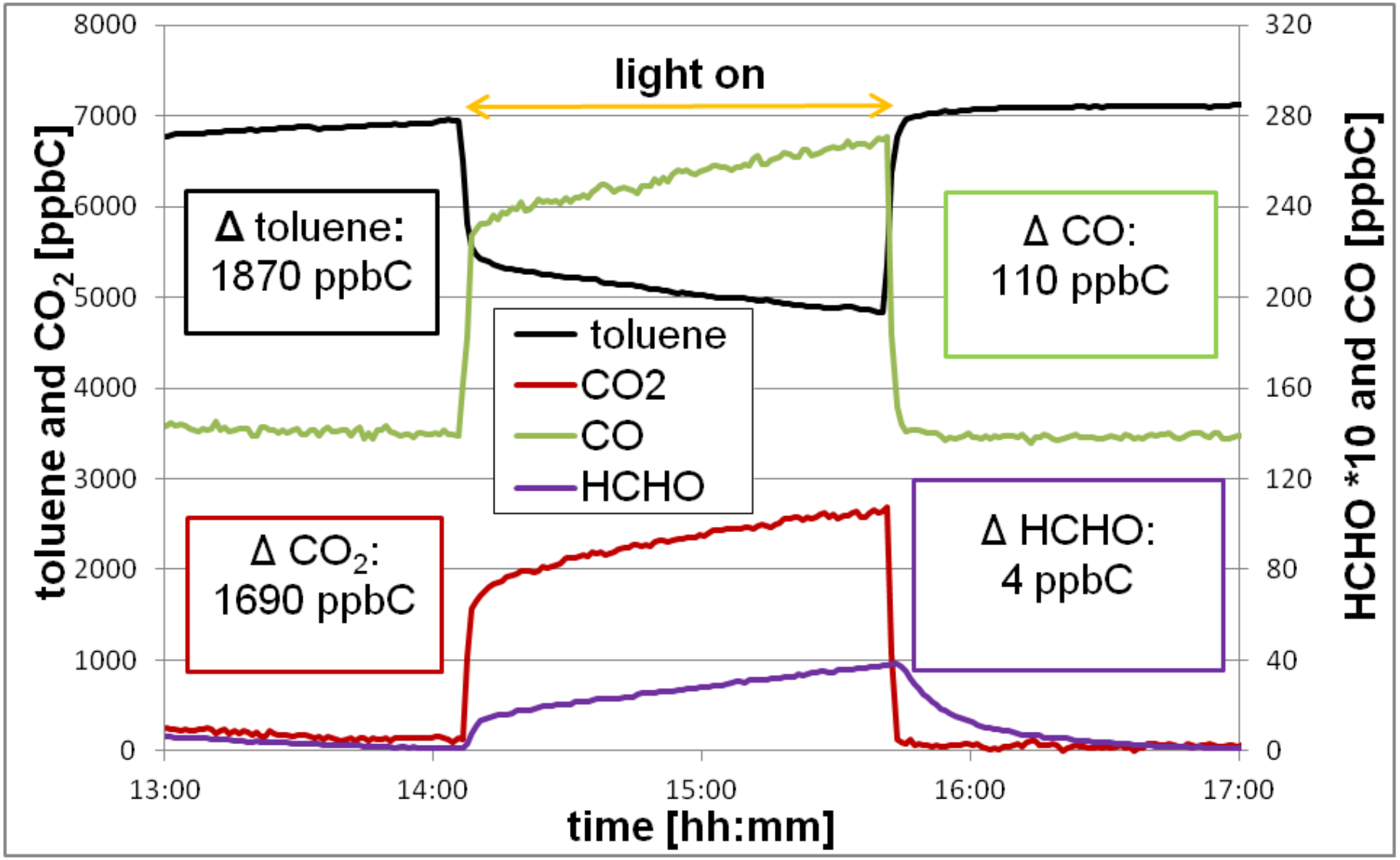
Uptake Coefficients (γ)

- γ independent of the surface to volume ratio S/V (⇔*k(VOC+TiO_2)*)

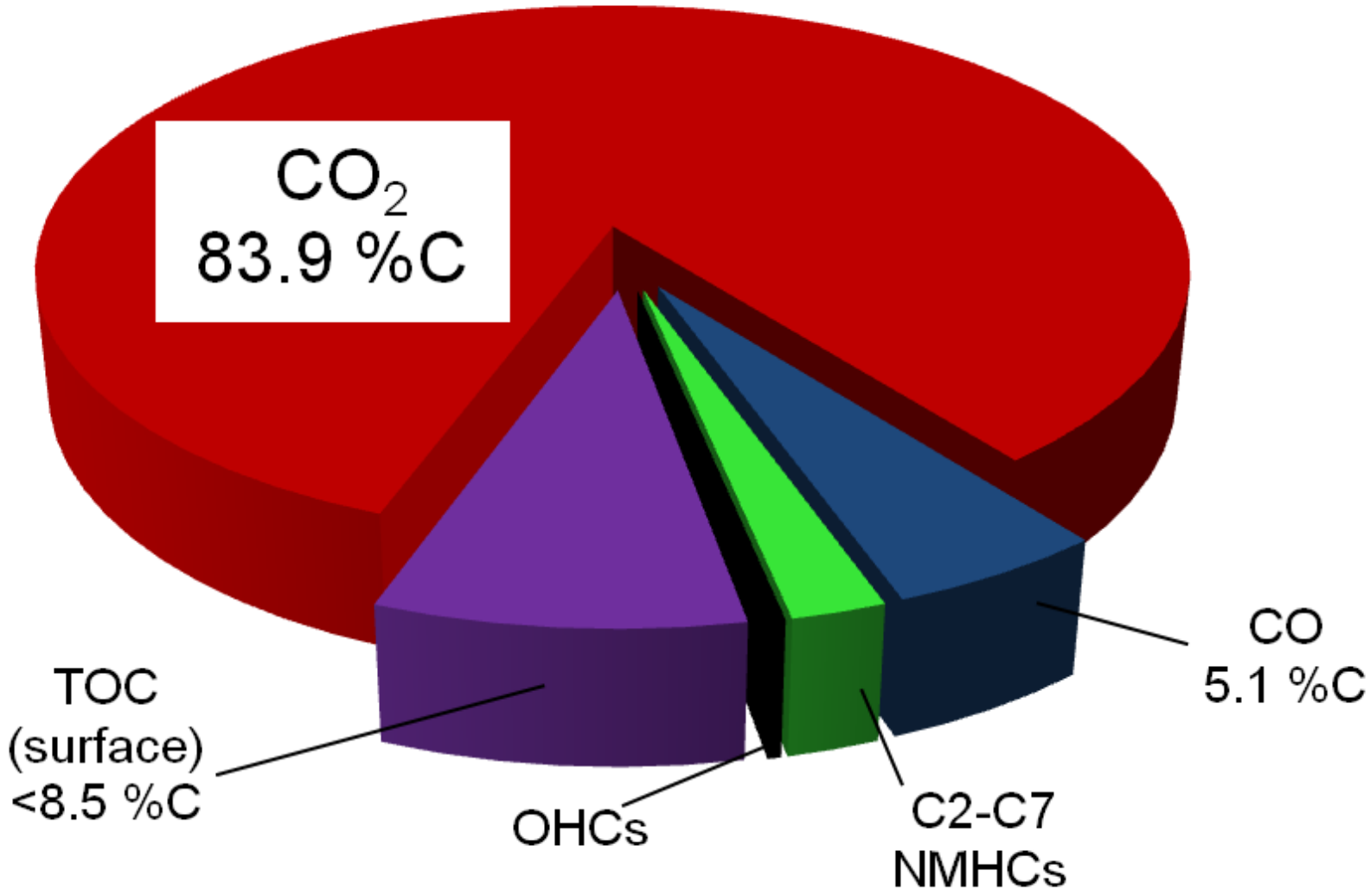
$$\gamma = \frac{4 \times k(VOC + TiO_2)}{\overline{v(VOC)} \times \frac{S}{V}}$$

- **γ(Toluene+TiO_2) = 1 × 10^{-5}**
- **γ(Benzene+TiO_2) = 5 × 10^{-6}**
- **γ(1-Butene+TiO_2) = 9 × 10^{-7}**
- **γ(iso-Pentane+TiO_2) = 4 × 10^{-7}**

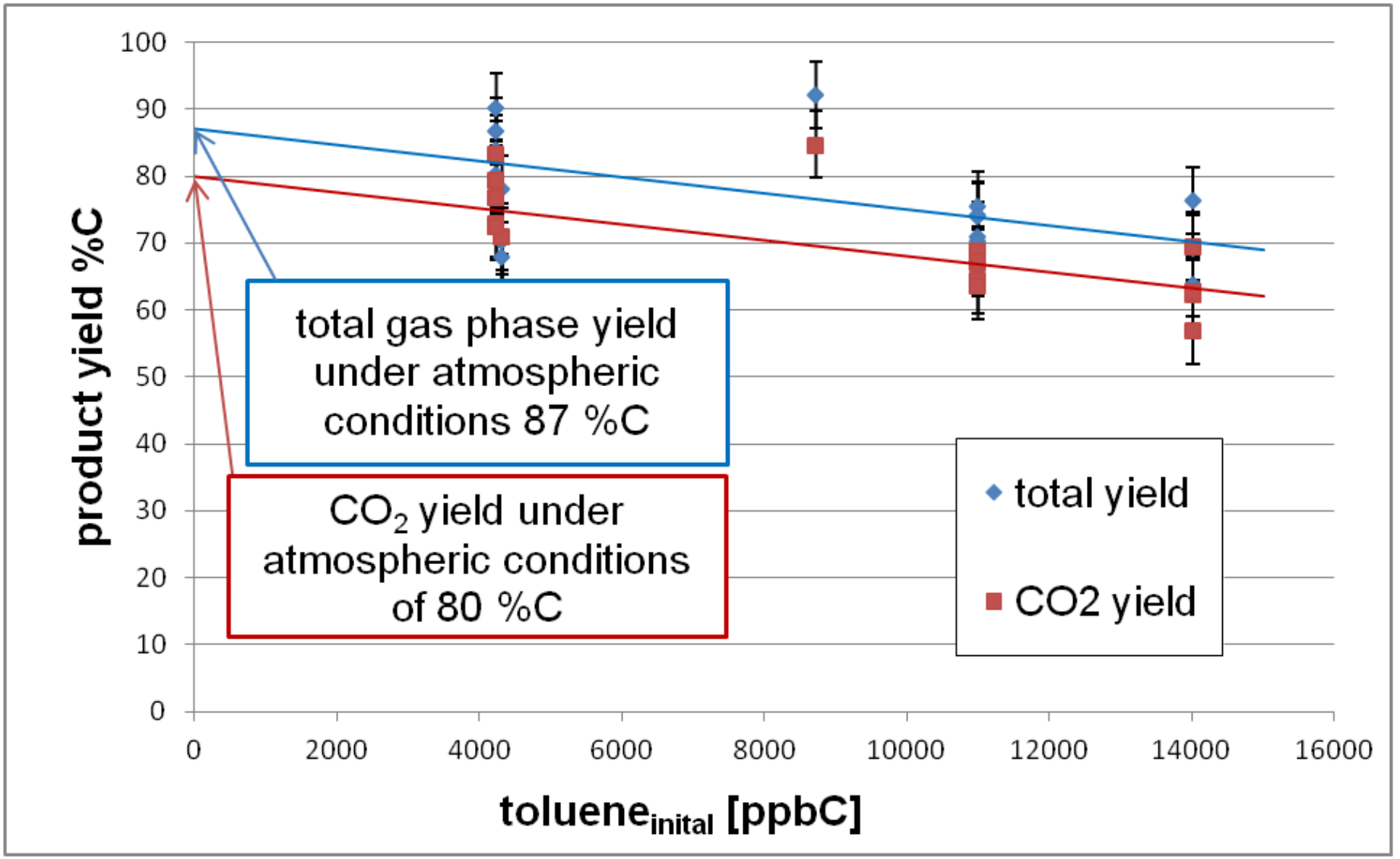
Products Formation: Toluene



Product yields (%C) for Toluene



Concentration Dependence of product yield



Postulated Reactions:

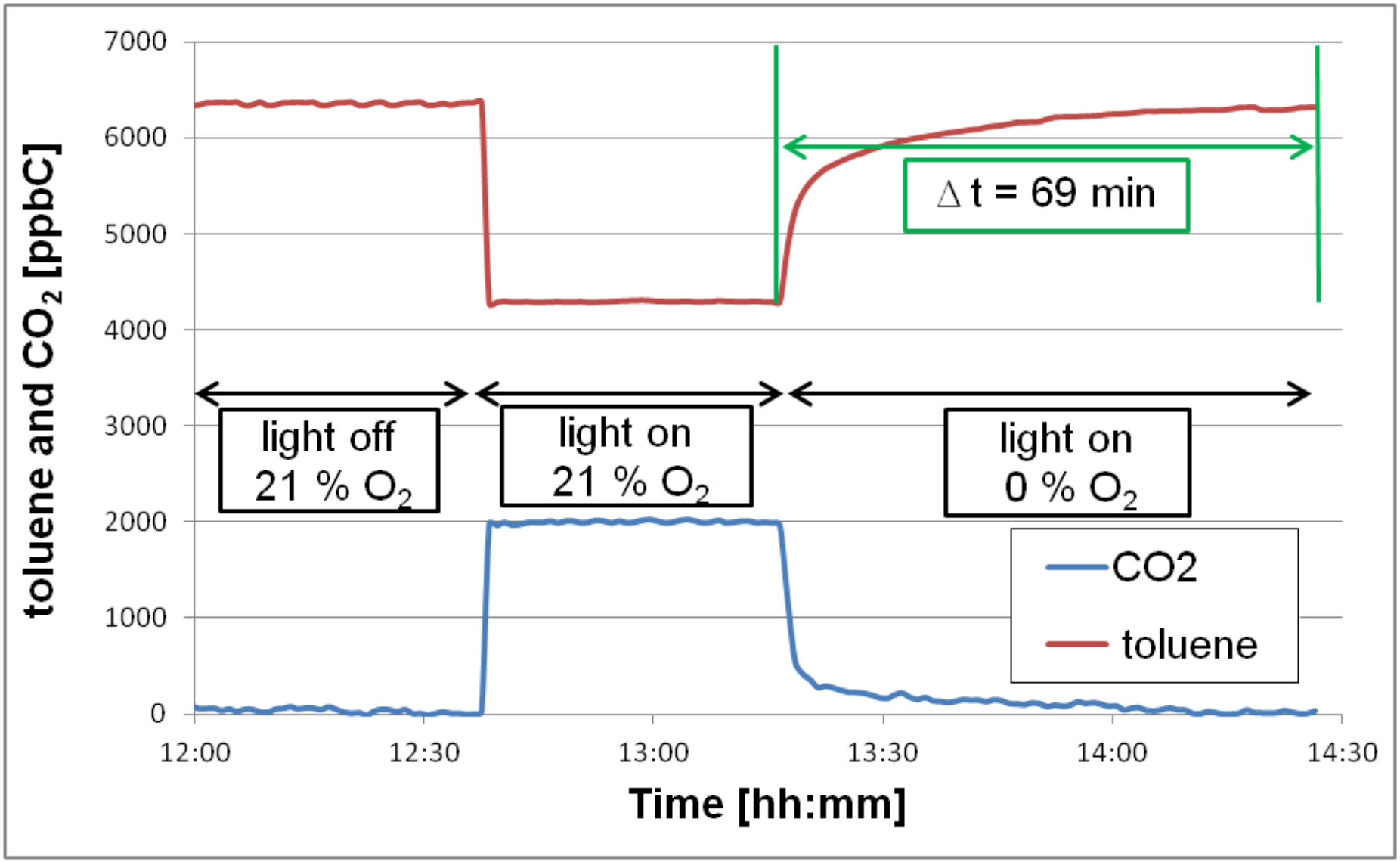
$VOC + O_2^-/O\ (TiO_2/h\upsilon/O_2) \rightarrow$ products

→oxygen dependence expected

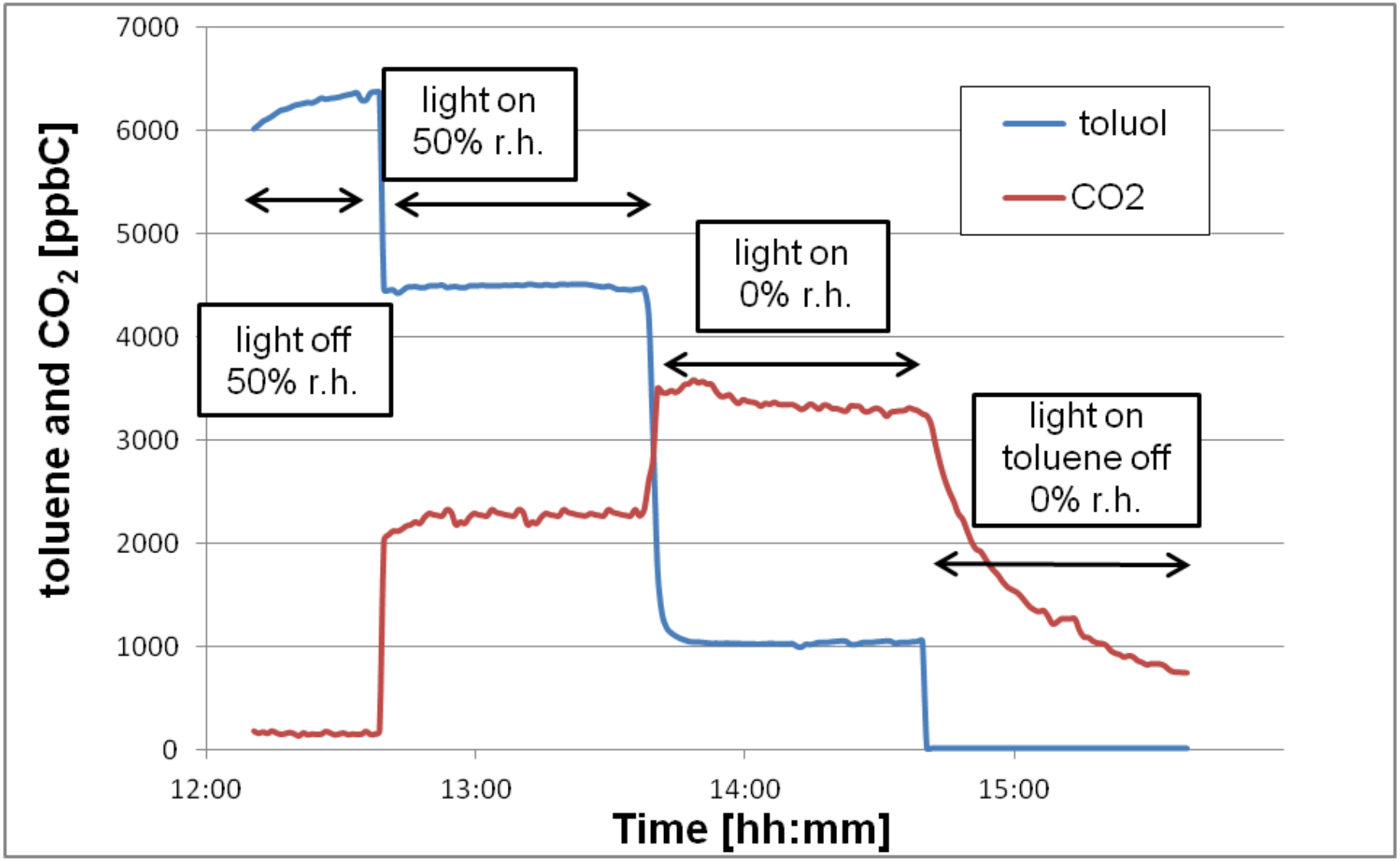
$VOC + OH\ (TiO_2/h\upsilon/H_2O) \rightarrow$ products

→ humidity dependence expected

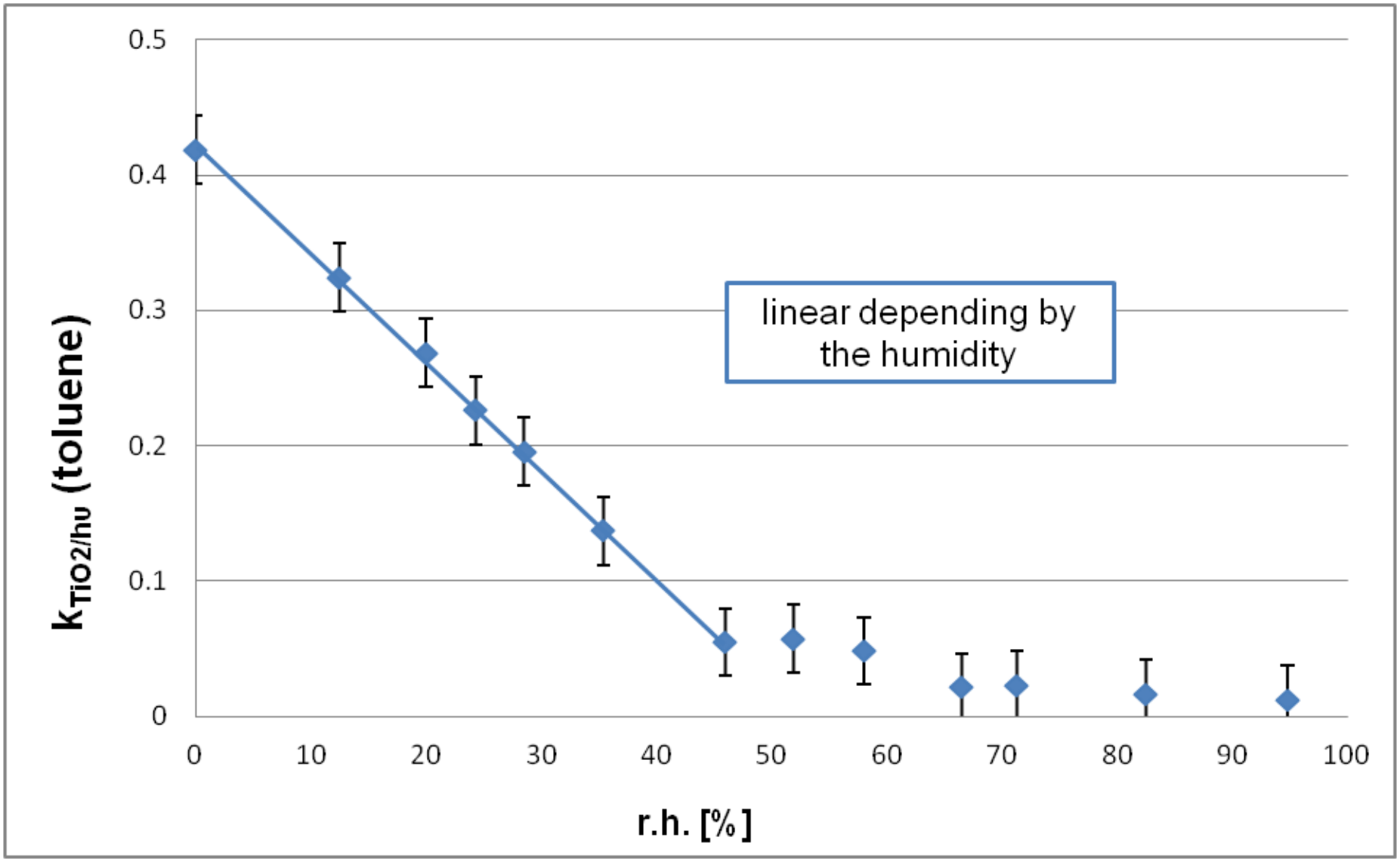
Oxygen Dependence:



Humidity Dependence:



K-Value Humidity Dependence:



Based on the humidity and oxygen dependencies:

$$\mathbf{VOC + O_2^-/O\ (TiO_2/h\upsilon/O_2) \rightarrow products}$$

proposed

Environmental Relevance

- Almost complete oxidation of the VOCs to CO_2
- Only small yields of NMHCs and OHCs
- Adsorbed TOC content <DL

➔ High CO_2 yield is not a problem:

- CO_2 also formed during the atmospheric degradation of VOCs
- Negligible source compared to other anthropogenic sources (combustion)

Environmental Relevance

➔ Product yields of NMHCs and OHCs are small compared to atmospheric degradation yields of VOCs

➔ TOC contamination of waste/ground water by rain wash-off not expected to be a problem:

- Small TOC yields
- Background contamination from other anthropo-genic sources is much higher
- Wet deposition of atmospheric OHCs and NMHCs (higher product yields!) more important

Summary

- All investigated VOCs (toluene, benzene, 1-butene, iso-pentane) photocatalytically degraded on the paint
- γ(toluene) > γ(benzene) > γ(1-butene) > γ(iso-pentane)
- Positive oxygen dependence
  → Oxidation via O_2^- or O-radicals
- Negative r.h. dependence
  → Oxidation via OH-radicals unlikely
- Similar products distribution for all VOCs:
  - CO_2 major product (60-84 %C),
  - CO minor product (3-5 %C)
  - Traces of NMHCs, OHCs
  - TOC < DL

Summary

- Degradation of VOCs in urban areas important:
  - Some VOCs directly harmful
  - ozone formation (summer smog) typically VOC-limited
  - Other harmful VOC oxidation products also reduced
    - SOA, PAN, nitrates,…

Open Question:

- What is the quantitative reduction in urban areas

  → Field measurements / model calculations

Acknowledgement

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Thank you for your attention!