



Kinetic investigations of by-products formed during photocatalytic oxidation of toluene at indoor air levels

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EMD : N. Locoge, F. Thévenet



European Symposium on
Photocatalysis 2009

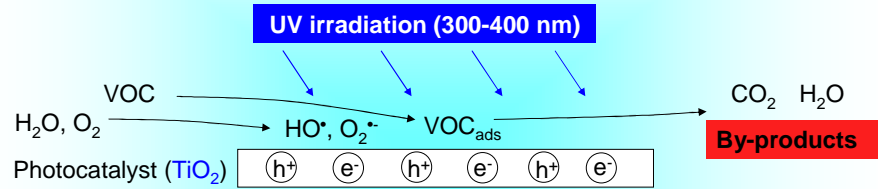
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Photocatalytic treatment

Photocatalytic oxidation : Volatil Organic Compounds (VOC) removal technic for Indoor Air Cleaning

Photocatalytic treatment

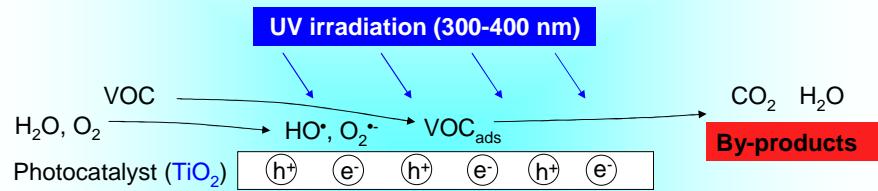
Photocatalytic oxidation : Volatil Organic Compounds (VOC) removal technic for Indoor Air Cleaning



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Photocatalytic treatment

Photocatalytic oxidation : Volatil Organic Compounds (VOC) removal technic for Indoor Air Cleaning

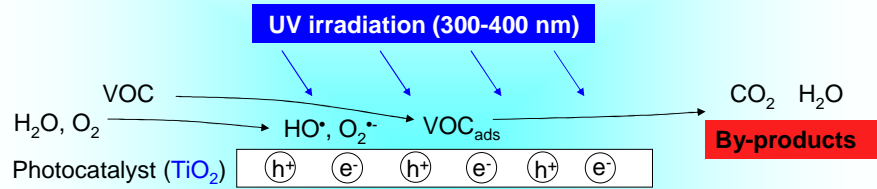


	Previous studies	Our study
VOC levels	ppm	ppb
Type of reactors	Continuous-flow reactors	Static reactor

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Photocatalytic treatment

Photocatalytic oxidation : Volatil Organic Compounds (VOC) removal technic for Indoor Air Cleaning



	Previous studies	Our study
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Selected VOC : toluene

- 1-100 ppb in indoor air
- Reference VOC

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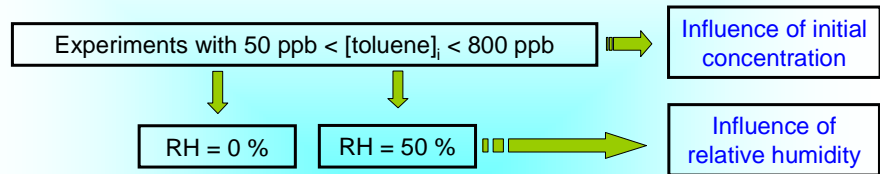
Objectives

Experiments with $50 \text{ ppb} < [\text{toluene}]_i < 800 \text{ ppb}$

Influence of initial concentration

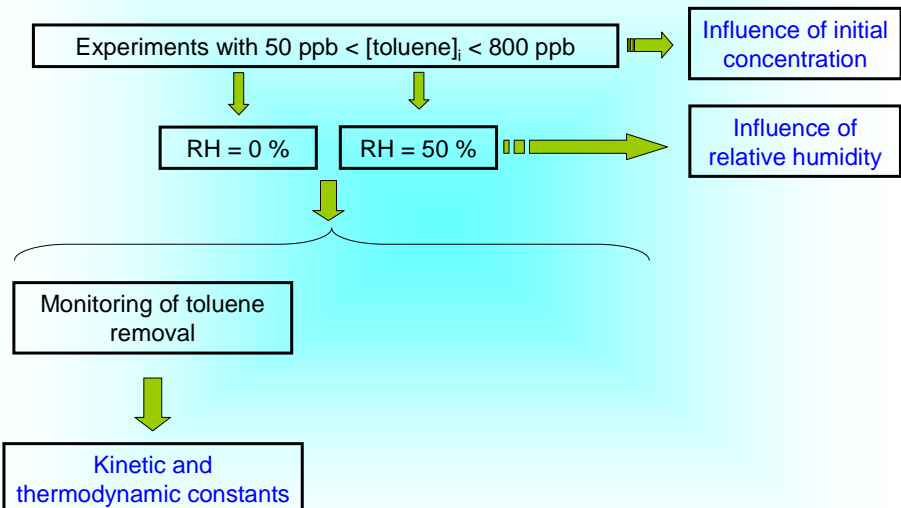
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Objectives



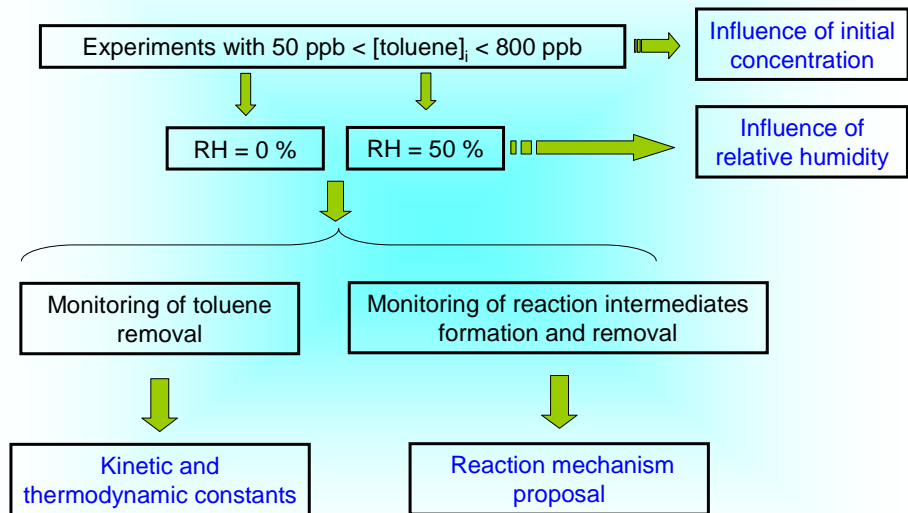
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Objectives



8

Objectives

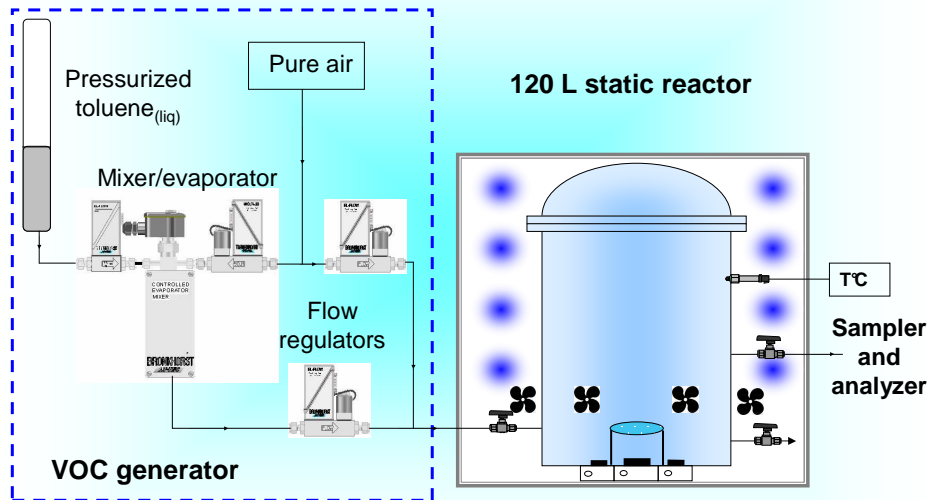


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Experimental set-up

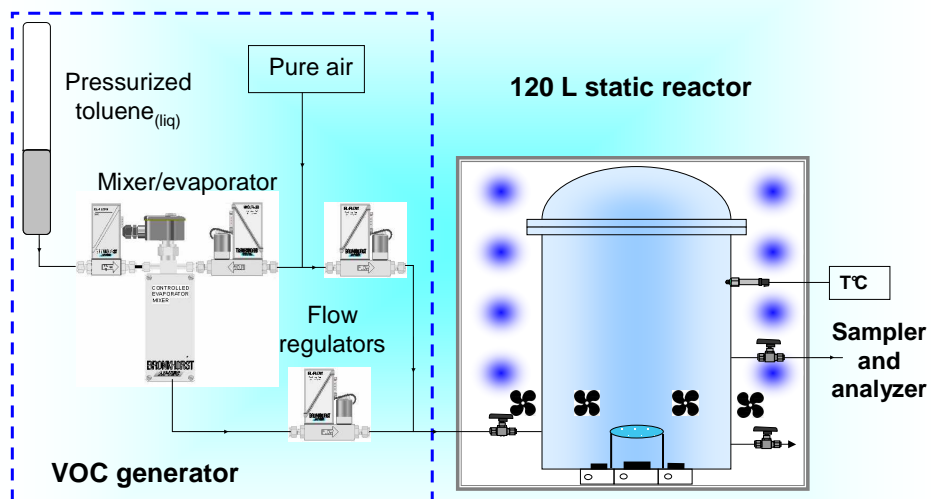
10

Experimental set-up



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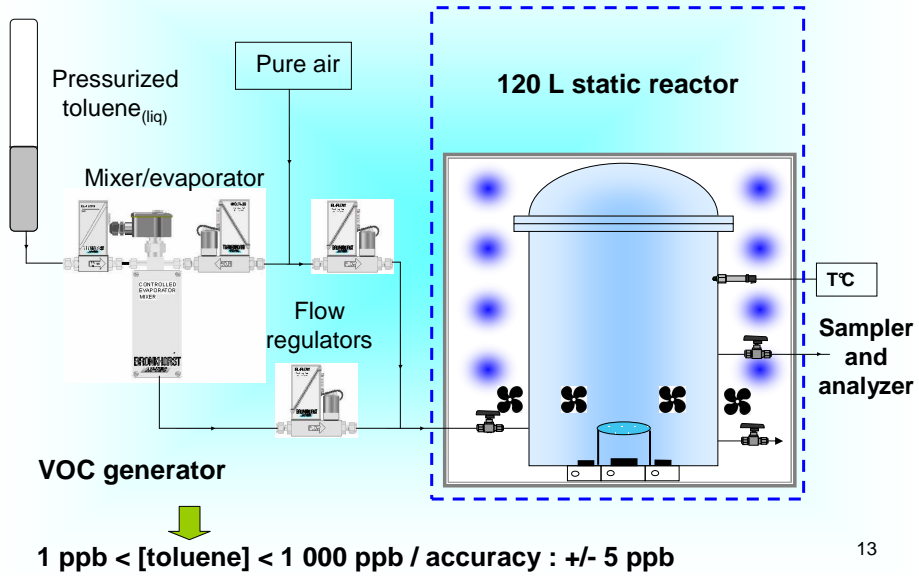
Experimental set-up



1 ppb < [toluene] < 1 000 ppb / accuracy : +/- 5 ppb

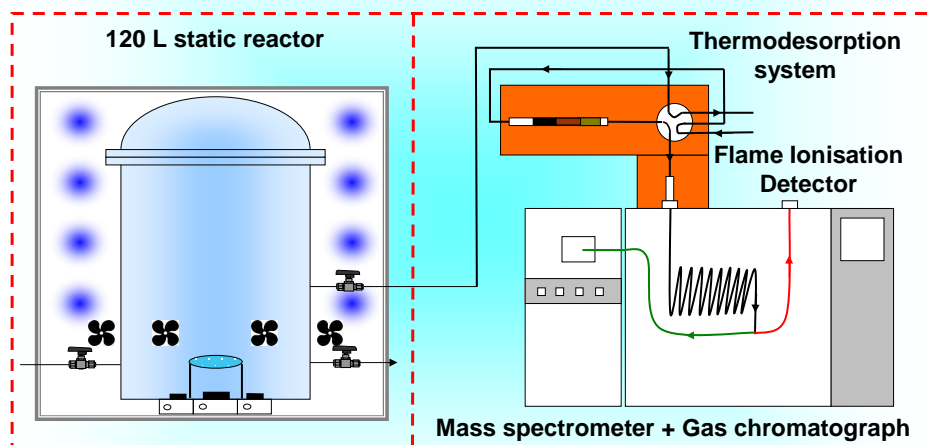
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Experimental set-up



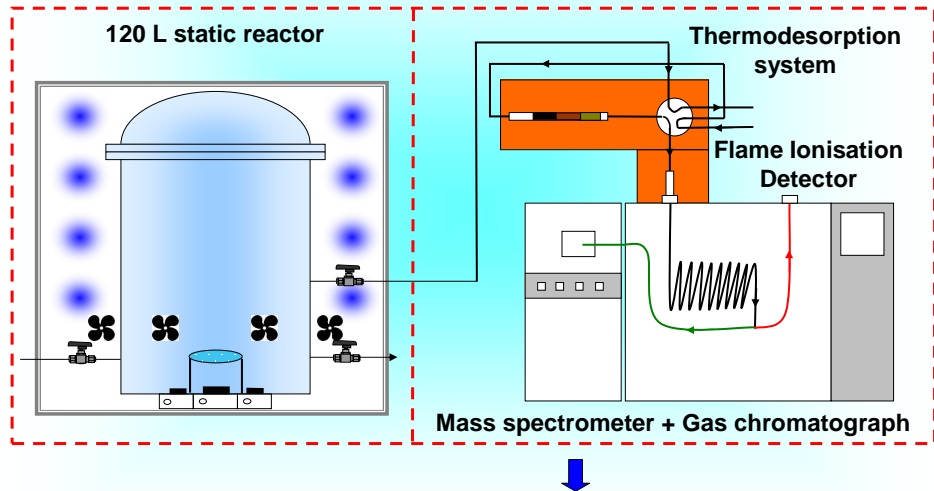
13

Experimental set-up



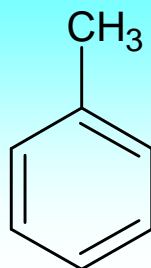
14

Experimental set-up



Detection limits < 100 pg ; 50 ppt for a sampling volume of 1 L ¹⁵

Toluene removal by photocatalytic oxidation at ppb level



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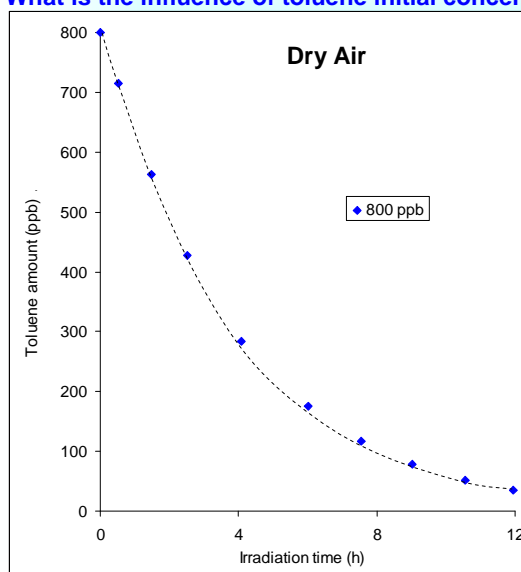
Toluene removal at ppb level

What is the influence of toluene initial concentration?

17

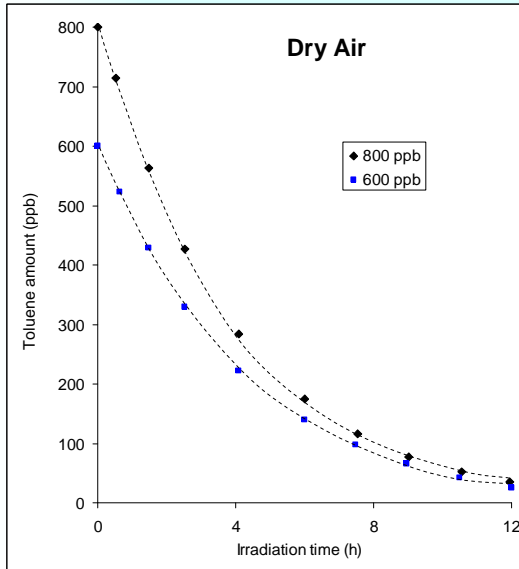
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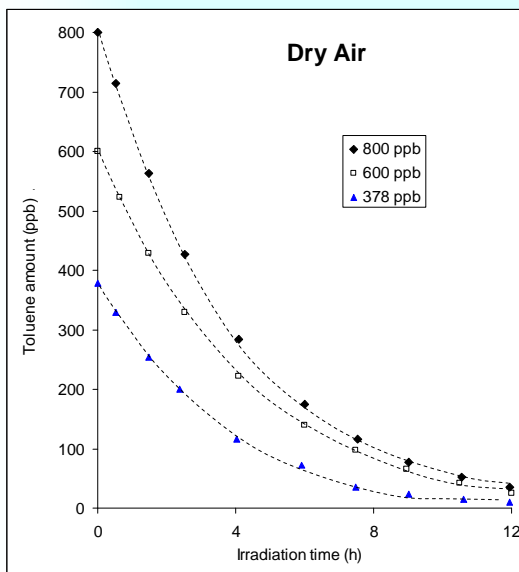
18

Toluene removal at ppb level



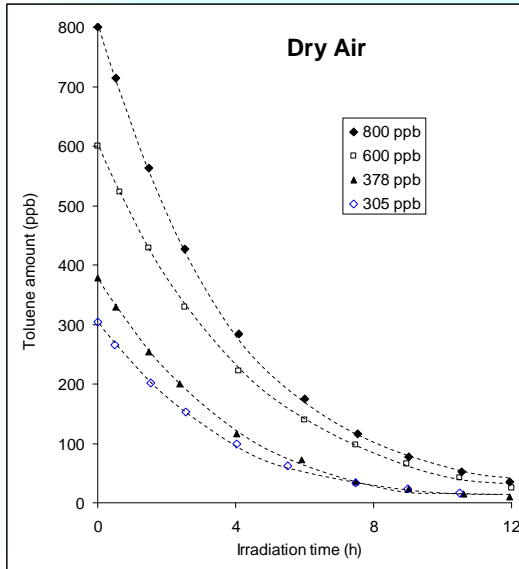
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Toluene removal at ppb level



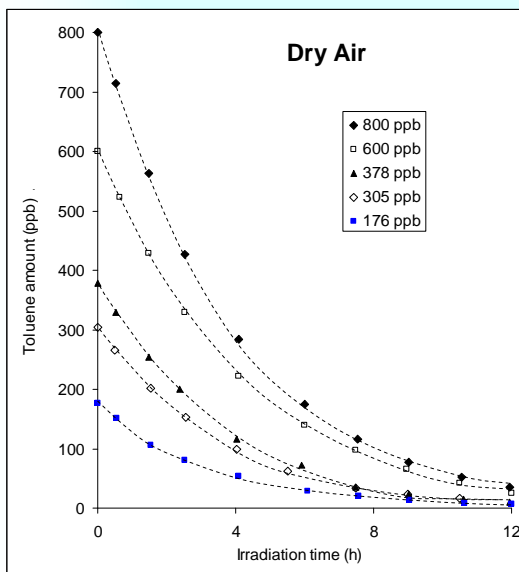
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Toluene removal at ppb level



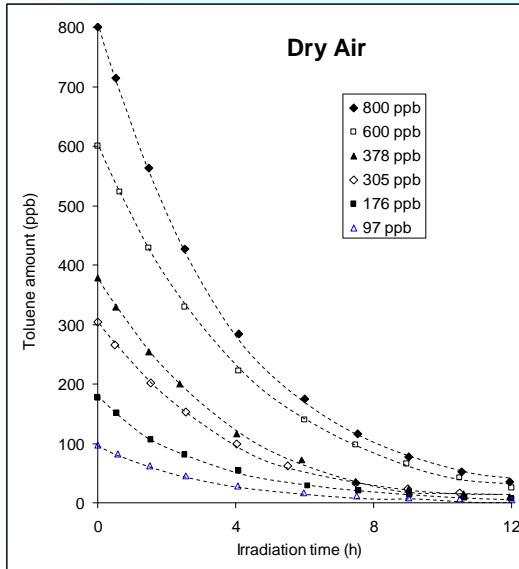
21

Toluene removal at ppb level



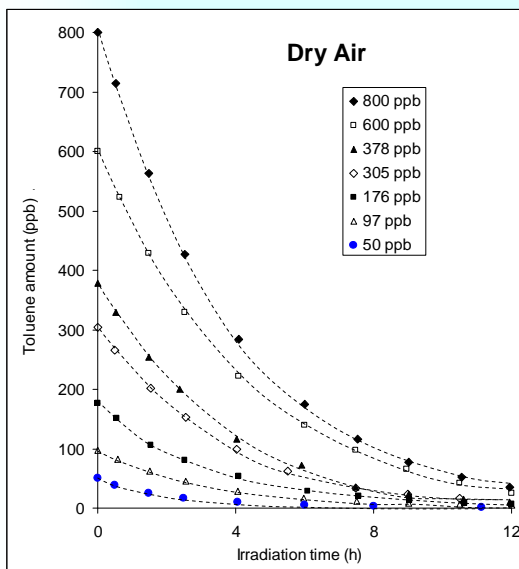
22

Toluene removal at ppb level



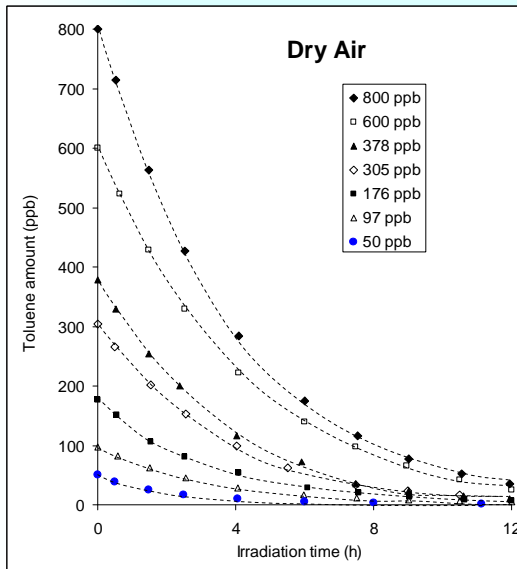
23

Toluene removal at ppb level



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Toluene removal at ppb level

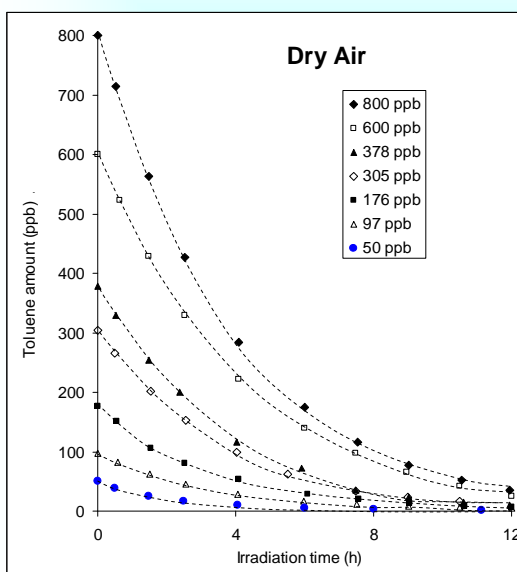


Reproducible experiments

→ No deactivation of the photocatalyst at ppb level

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Toluene removal at ppb level



Reproducible experiments

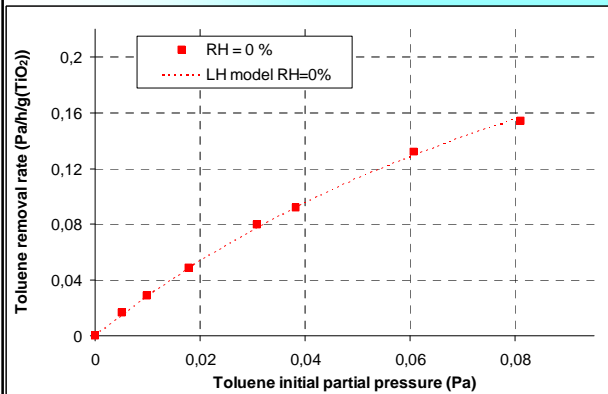
→ No deactivation of the photocatalyst at ppb level

$$r_{\text{tol}(i)} = f(P_{\text{tol}(i)}) ?$$

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Toluene removal at ppb level

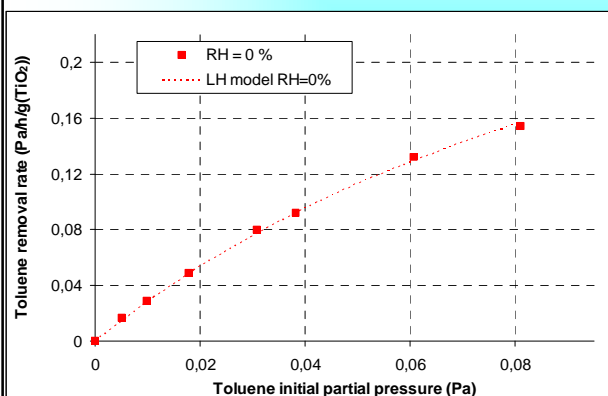
$$r_{\text{tol}(i)} = f(P_{\text{tol}(i)})$$



27

Toluene removal at ppb level

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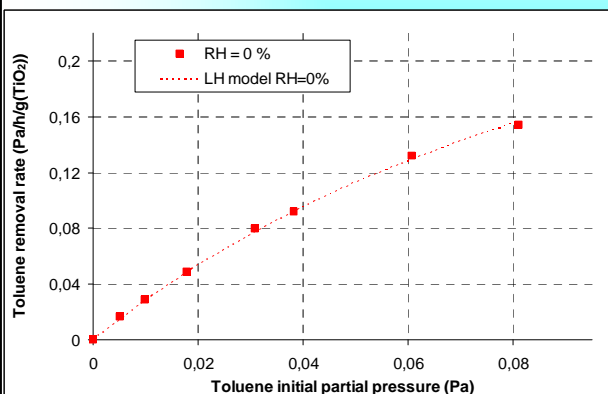
Experimental data can be fitted by **Langmuir-Hinshelwood** model at ppb level

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Toluene removal at ppb level

$$r_{\text{tol}(i)} = f(P_{\text{tol}(i)})$$

Experimental data can be fitted by **Langmuir-Hinshelwood** model at ppb level



	Dry
$k(\text{Pa}/\text{h}/\text{g}^{-1})$	0,42
$K(\text{Pa}^{-1})$	7,47

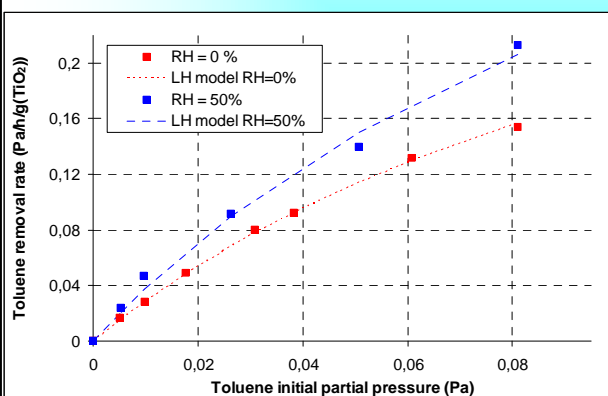
k : kinetic rate ; K : adsorption rate

29

Toluene removal at ppb level

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Experimental data can be fitted by **Langmuir-Hinshelwood** model at ppb level



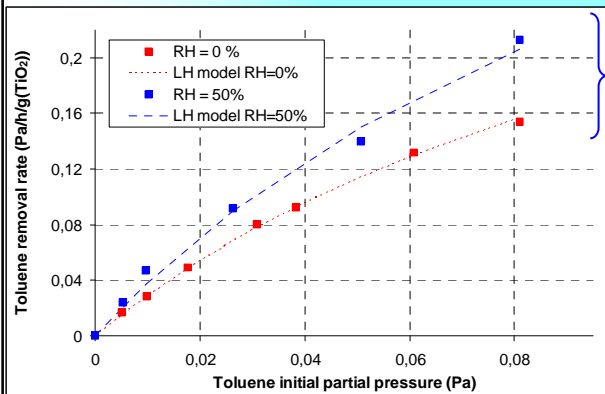
	Dry	Wet
$k(\text{Pa}/\text{h}/\text{g}^{-1})$	0,42	0,55
$K(\text{Pa}^{-1})$	7,47	7,41

k : kinetic rate ; K : adsorption rate

30

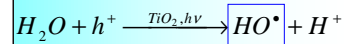
Toluene removal at ppb level

$$r_{\text{tol}(i)} = f(P_{\text{tol}(i)})$$



Experimental data can be fitted by **Langmuir-Hinshelwood** model at ppb level

→ Same effect of H₂O_(g) at ppm and ppb level

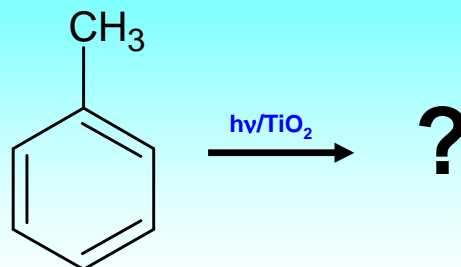


	Dry	Wet
$k(Pa/h/g^{-1})$	0,42	0,55
$K(Pa^{-1})$	7,47	7,41

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Toluene reaction intermediates at ppb level



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Toluene photooxidation intermediates

Which compounds are formed during the removal of toluene ?

➤ 16 similar intermediates under **dry** air and **wet** air (RH = 50 %)

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Toluene photooxidation intermediates

Which compounds are formed during the removal of toluene ?

➤ 16 similar intermediates under **dry** air and **wet** air (RH = 50 %)

Carbonyls

Acetaldehyde
Acroleine
Acetone
Propanaldehyde
Methyl vinyl ketone
Butyraldehyde
2-butanone
Valeraldehyde
Heptanal

34

Toluene photooxidation intermediates

Which compounds are formed during the removal of toluene ?

➤ **16 similar intermediates** under **dry** air and **wet** air (RH = 50 %)

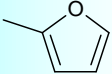
Carbonyls	Aromatics
Acetaldehyde	Benzene
Acroleine	Phenol
Acetone	Benzaldehyde
Propanaldehyde	o-cresol
Methyl vinyl ketone	p+m-cresol
Butyraldehyde	
2-butanone	
Valeraldehyde	
Heptanal	

35

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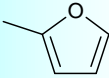
Carbonyls	Aromatics	2-methylfuran
Acetaldehyde	Benzene	
Acroleine	Phenol	
Acetone	Benzaldehyde	
Propanaldehyde	o-cresol	
Methyl vinyl ketone	p+m-cresol	
Butyraldehyde		
2-butanone		
Valeraldehyde		
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36

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Butyraldehyde		
2-butanone		
Valeraldehyde		
Heptanal		



Same diversity of compounds under static conditions than *Sleiman et al. (2009)* & *Mo et al. (2009)*

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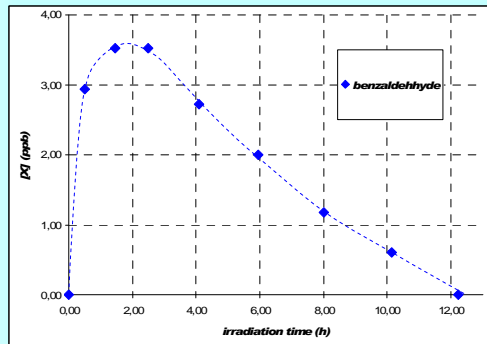
Toluene photooxidation intermediates

What is the temporal ordering of intermediates formation ?

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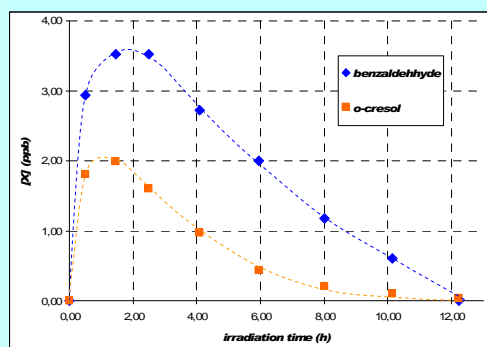


Aromatics : 1h < [max] < 2h → complet removal

39

Toluene photooxidation intermediates

What is the temporal ordering of intermediates formation ?

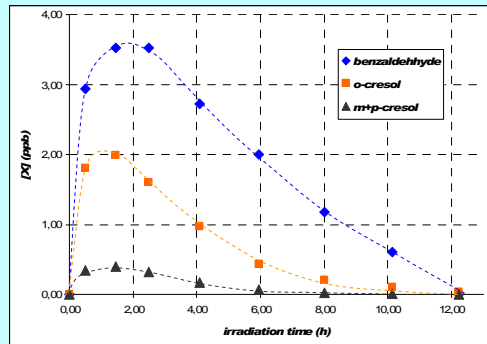


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40

Toluene photooxidation intermediates

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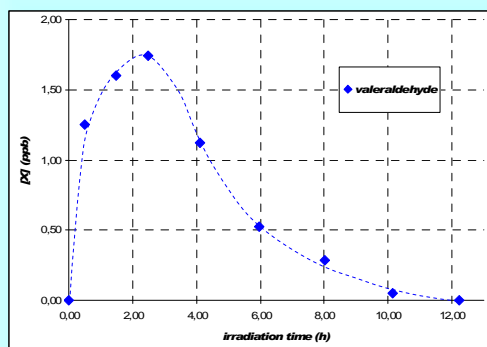


Aromatics : 1h < [max] < 2h → complet removal

41

Toluene photooxidation intermediates

What is the temporal ordering of intermediates formation ?

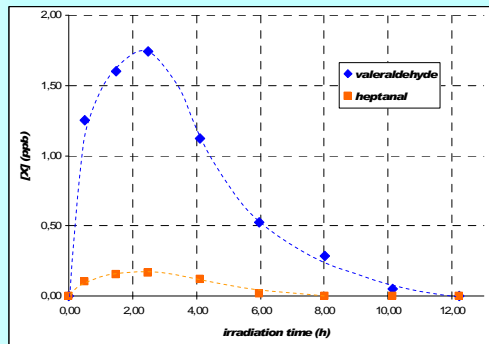


Aldehydes : 2h < [max] < 4h → complet removal

42

Toluene photooxidation intermediates

What is the temporal ordering of intermediates formation ?

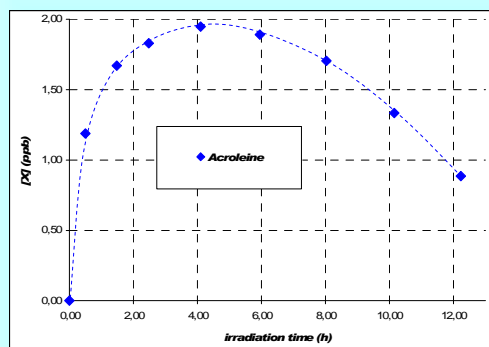


Aldehydes : $2\text{h} < [\text{max}] < 4\text{h} \rightarrow$ complet removal

43

Toluene photooxidation intermediates

What is the temporal ordering of intermediates formation ?

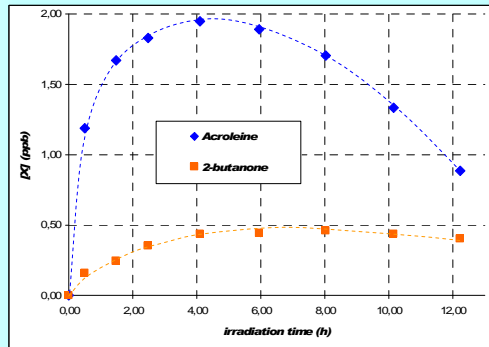


shorter carbonyls \rightarrow persistant compounds

44

Toluene photooxidation intermediates

What is the temporal ordering of intermediates formation ?

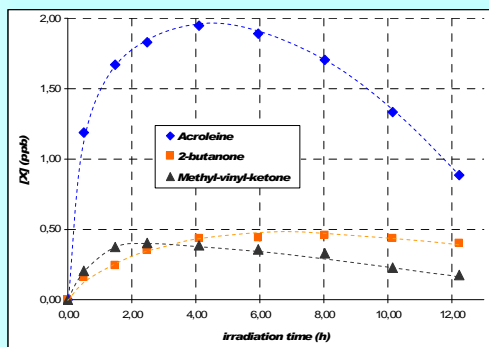


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45

Toluene photooxidation intermediates

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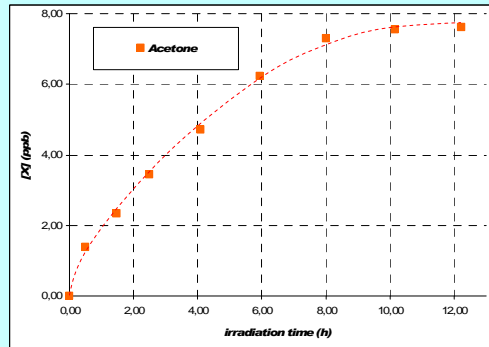


shorter carbonyls → persistent compounds

46

Toluene photooxidation intermediates

What is the temporal ordering of intermediates formation ?



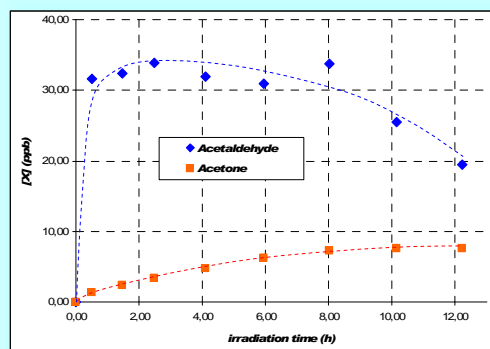
High amount formation, no removal noticed

→ Accumulation into indoor air...?

47

Toluene photooxidation intermediates

What is the temporal ordering of intermediates formation ?



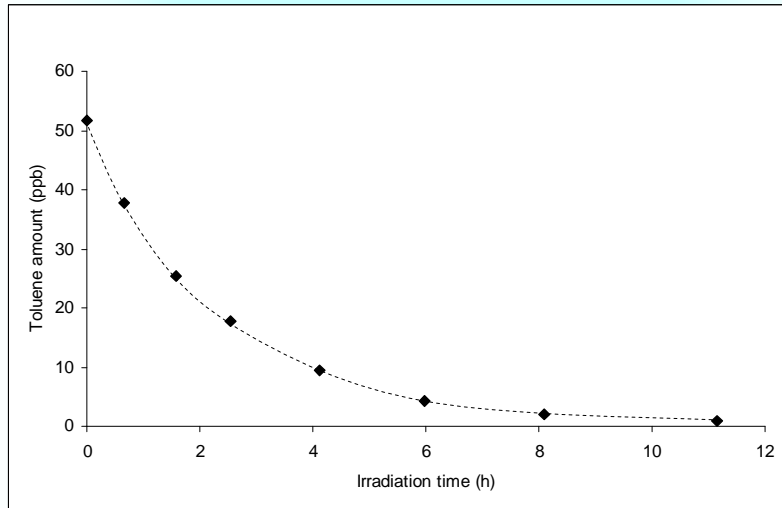
High amount formation + difficult removal

→ Accumulation into indoor air...?

48

Toluene photooxidation intermediates

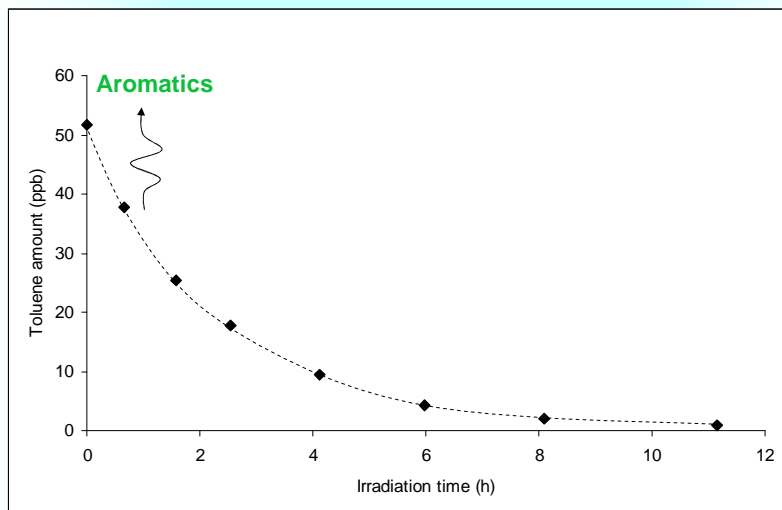
What is the temporal ordering of intermediates formation ?



49

Toluene photooxidation intermediates

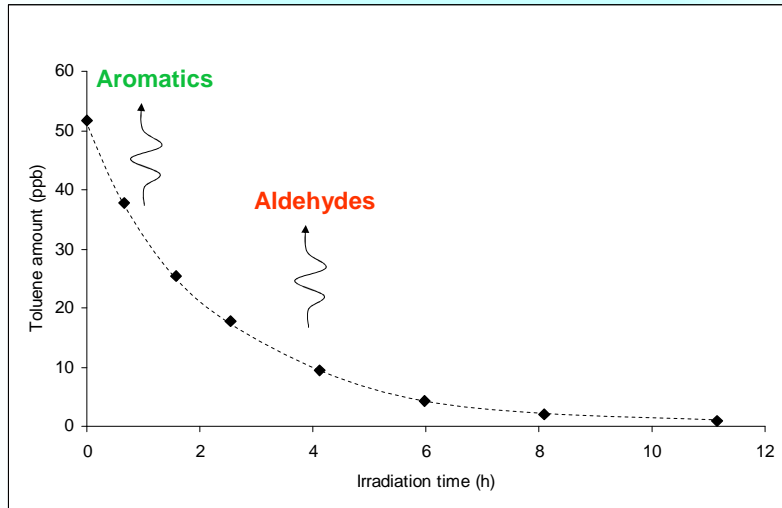
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50

Toluene photooxidation intermediates

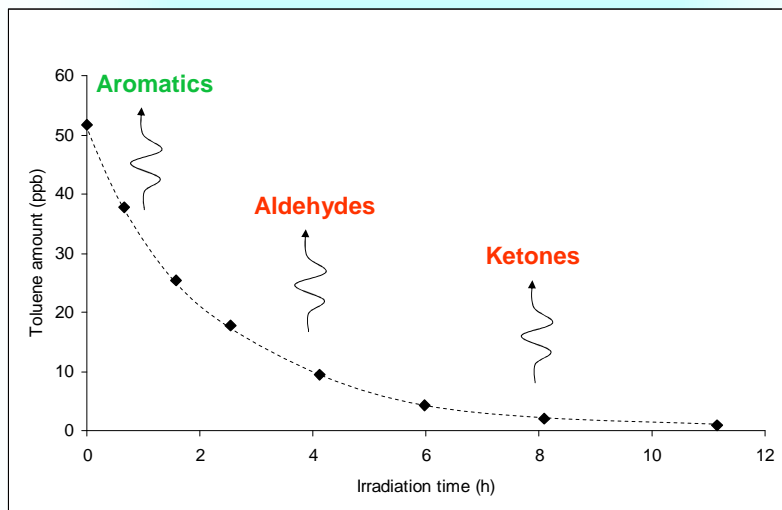
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51

Toluene photooxidation intermediates

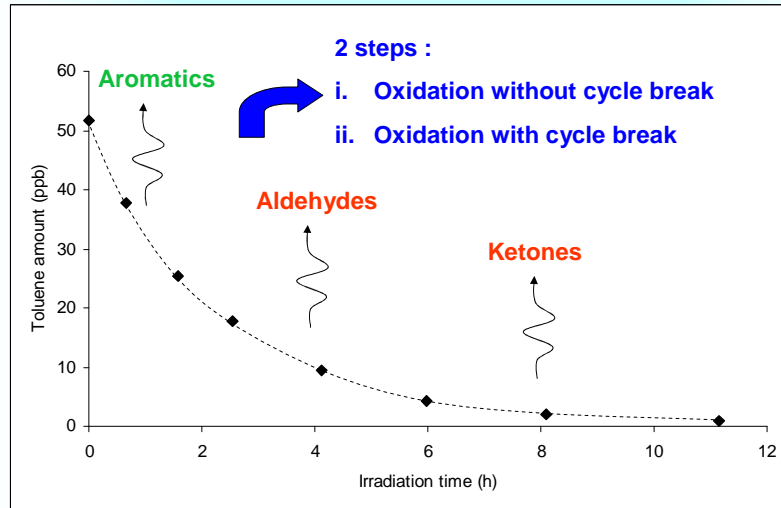
What is the temporal ordering of intermediates formation ?



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Toluene photooxidation intermediates

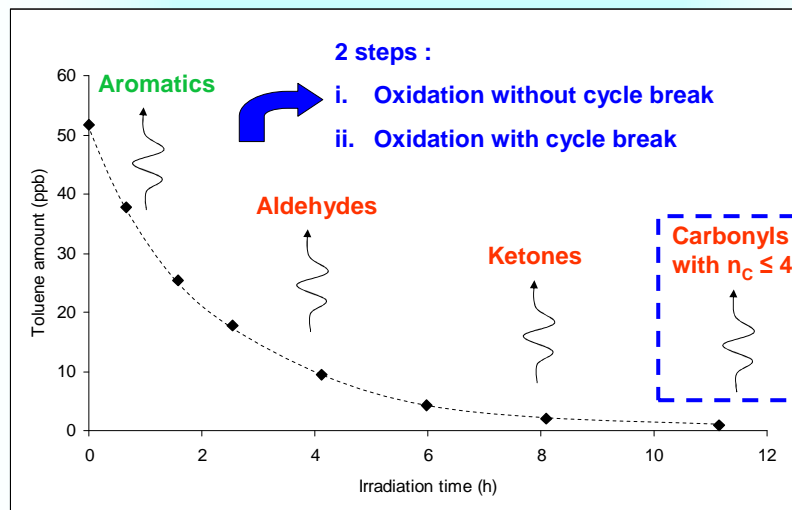
What is the temporal ordering of intermediates formation ?



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Toluene photooxidation intermediates

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Toluene photooxidation intermediates

What is the influence of the initial concentration of toluene on intermediate amounts ?

55

Toluene photooxidation intermediates

What is the influence of the initial concentration of toluene on intermediate amounts ?

- Comparison between the maximum amounts formed with two initial toluene concentrations

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Toluene photooxidation intermediates

What is the influence of the initial concentration of toluene on intermediate amounts ?

➤ Comparison between the maximum amounts formed with two initial toluene concentrations

$$x = \frac{C_i(\text{toluene})}{C'_i(\text{toluene})} \times \frac{C'_{\max}(\text{intermediate})}{C_{\max}(\text{intermediate})}$$

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Toluene photooxidation intermediates

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$$C_i(\text{toluene}) = 800 \text{ ppb} \quad C'_i(\text{toluene}) = 50 \text{ ppb}$$



$$\frac{C_i(\text{toluene})}{C'_i(\text{toluene})} = 16$$

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Theoretically :

$$x = 1$$

59

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Theoretically :

$$x = 1$$

Acetaldehyde	6
Acroleine	7
Acetone	12
Methyl vinyl ketone	5
Butyraldehyde	8
2-butanone	13
Valeraldehyde	5
Heptanaldehyde	4
Benzene	5
Benzaldéhyde	1
o-cresol	1
p+m-cresol	1

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Toluene photooxidation intermediates

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➤ Comparison between the maximum amounts formed with two initial toluene concentrations

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Theoretically :
 $x = 1$

Only primary intermediates are
proportional to initial
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Conclusion

Photocatalytic oxidation of toluene / $C_i = 50-800$ ppb / static reactor

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Well fitting with Langmuir-Hinshelwood model
even at ppb level

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Enhancing of the removal rate of
toluene with water

Photocatalytic oxidation of toluene / $C_i = 50-800$ ppb / static reactor

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Enhancing of the removal rate of
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Photocatalytic oxidation of toluene / $C_i = 50-800$ ppb / static reactor

No influence of humidity on the nature of
reaction intermediates
at ppb level

65

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Photocatalytic oxidation of toluene / $C_i = 50-800$ ppb / static reactor

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First step of degradation : aromatic reactions
→ formation of benzaldehyde and cresols

66

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First step of degradation : aromatic reactions
→ formation of benzaldehyde and cresols

Second step of degradation : aliphatic reactions
→ formation of carbonyls

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Conclusion

Photocatalytic oxidation of toluene / $C_i = 50-800$ ppb / static reactor



Further investigations on others compounds and on mixtures

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**Thank you for
your attention**

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