



# Toluene photocatalytic oxidation at ppbv levels: Kinetic investigation and carbon balance determination

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## ABSTRACT

An investigation of toluene photocatalytic oxidation was conducted with initial concentrations of toluene ranging from 50 to 800 ppbv under dry and wet (50% RH) atmosphere in order to characterize photocatalysis performances close to indoor air conditions. A batch reactor system was developed in order to perform kinetic studies of (i) toluene removal, (ii) organic reaction intermediate formation and removal, (iii) CO and CO<sub>2</sub> formation, at ppbv levels. The monitoring of CO and CO<sub>2</sub> produced by a photocatalytic reaction in the air with ppbv levels of pollutant is reported for the first time. It appears that toluene removal follows, even at ppbv levels, a pseudo first order kinetic slightly improved by the presence of water vapour (50% RH). The determination of reaction intermediate temporal profiles confirmed that oxidized aromatic compounds (benzaldehyde, cresols) are toluene primary reaction intermediates. The fact that no benzoic acid was evidenced in the gas phase, and that benzaldehyde maximum concentration remains below 4 ppbv indicate that several consecutive oxidation steps take place in the adsorbed phase with a low desorption of reaction intermediate. The diversity of aliphatic reaction intermediates obtained after toluene ring opening is coherent with former results obtained at ppmv initial levels of toluene. Nevertheless, the removal of the lightest carbonyls (acetone, acetaldehyde and formaldehyde) is not observed within 14 h of reaction. Carbon mass balance calculations performed with all the quantified gas phase reaction intermediates evidenced that those compounds represent only from 1 to 1.5%. This portion is almost constant during the whole oxidation process. The precise determination of CO and CO<sub>2</sub> concentrations gives a good overview of the oxidation/mineralization process. CO and CO<sub>2</sub> measurements evidenced that the presence of water vapour (50% RH) considerably improves the formation of CO<sub>2</sub> corresponding to a better mineralization of organic matter and an improved conversion of CO into CO<sub>2</sub>. Temporal profiles of CO<sub>2</sub> concentration reveal that CO<sub>2</sub> formation rate is highly dependent on the nature of the compounds to be treated. Between 10 and 12 h of reaction, corresponding to 95% conversion of toluene, CO and CO<sub>2</sub> represent only from 25 to 35% of the carbon mass balance. If the reaction is performed on longer times, the mineralization percentage constantly increases until 23 h of irradiation, mainly corresponding to oxidation of compounds adsorbed on photocatalyst surface. After 22 h of irradiation, the mineralization (CO + CO<sub>2</sub>) finally exceeds 70% of the carbon mass balance.

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## 1. Introduction

People spend more than 80% of their lifetime in indoor environment. Over the last 25 years, health complaints related to poor indoor air quality have dramatically increased [1]. Therefore, indoor air pollution has become a major public health concern. Indoor air contaminants can be classified according to three main categories: organic/inorganic chemical species, particulate matters, and molds. They are responsible for allergic reactions, headache, eye, nose and

throat irritation, dry cough, nausea and, more generally, can trigger the sick building syndrome (SBS) or building related illness. Volatile organic compounds (VOC) represent the major group of indoor air contaminants [2]. Sources of VOC have been attributed to outdoor air, cooking, carpets, desks, paintings, ceilings [3,4], for instance. Concentrations of VOC can build up because of the low turnover rate of air in modern buildings sealed by high efficiency thermal insulation devices. Photocatalytic oxidation has been developed toward VOC treatment for several years. Since 1995, the number of manuscripts per year on photocatalytic indoor air treatment has been continuously increasing, reaching 60 articles only for the year 2007 [5]. The number of patents followed the same tendency, with almost 180 patents in 2007 dealing with photocatalytic

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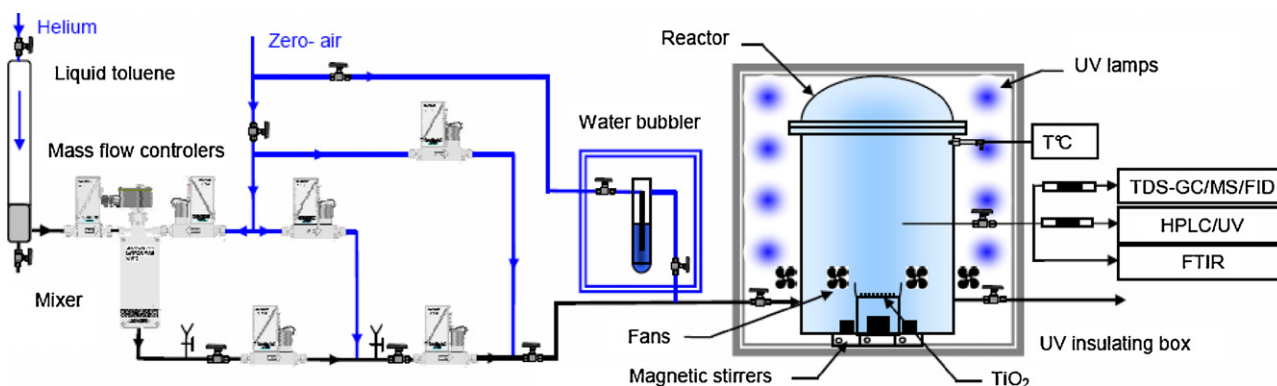


Fig. 1. Experimental set up scheme.

air treatment devices. This technology has already shown its efficiency toward VOC abatement, however, two points have still to be clarified: (i) photocatalytic oxidation of VOC has been mainly investigated for several years at ppmv levels whereas typical indoor pollutant concentrations range from 100 ppt to 100 ppbv [6]; (ii) photocatalytic oxidation potentially mineralizes VOC into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , but intermediates can also be formed and accumulate in the air even at ppbv levels of initial contaminants. Our investigations are based on those obstacles.

Toluene is one of the most investigated model pollutant in the photocatalytic oxidation studies. It has been recommended as model pollutant for photocatalytic system performance evaluation in the AFNOR standard XP-B44-013 developed by a French normalization group [7]. During an investigation on indoor air quality in various German cities, Schneider et al. [8] reported that toluene indoor air concentrations are from 5 to 7 times higher than outdoor. The main sources of toluene in indoor air are paintings and tobacco smoke. Concentrations are sensitive to seasons and indoor temperature. Numerous authors worked on toluene degradation; they generally perform photocatalytic reactions at ppmv levels [9–11]. Few studies report the treatment of toluene at typical indoor air levels, they mainly focused on the abatement of the initial pollutant in plug flow reactors [12–15]. Under those conditions authors explored the influence of toluene initial concentration, relative humidity and UV photon flux on toluene removal rate. The formation of reaction intermediates is not investigated excepted by Sleiman et al. [16]. Authors succeeded in identifying and quantifying various aromatic and aliphatic toluene reaction intermediates and by-products using an annular flow-through reactor with toluene initial concentrations ranging from 20 to 400 ppbv. Nevertheless, their steady state approach did not allow them to investigate the kinetic of formation/removal of the various reaction intermediates. Moreover, this attempt to evaluate the mineralization of toluene ( $\text{CO}$  and  $\text{CO}_2$  formation) at ppbv levels with PDPID detector required to operate photocatalytic reactions in helium with only 2% of  $\text{O}_2$ . Those conditions were far from indoor air typical conditions, moreover,  $\text{O}_2$  partial pressure could greatly influence the mineralization of gaseous organic substances [17,18].

The present work investigates the photocatalytic oxidation of toluene under real indoor air levels and conditions. A kinetic approach is developed using a batch reactor. The main objective of this study is to describe the temporal evolution of the reaction chamber composition regarding simultaneously (i) toluene removal, (ii) reaction intermediates formation and removal, (iii) mineralization through  $\text{CO}_2$  and  $\text{CO}$  production. This approach leads to the determination of toluene photocatalytic oxidation carbon balance at ppbv levels. Experiments are performed at two different relative humidities: 0% and 50% in order to evaluate the influence of water vapor on the ppbv level oxidation processes.

## 2. Experimental

An appropriate experimental device was especially developed for the experiments. It can be divided into three parts: (i) VOC generator system at ppbv range, (ii) reaction chamber, (iii) analytical devices for VOC analysis at ppbv range.

Air used for all experiments was supplied by a Claind AZ-2020 zero air generator and a Pressure Swing Adsorption (PSA) system (Thermo-Electron and Domnik Hunter). The first step consists in a catalytic treatment unit permitting the oxidation of VOC present in the air flow into  $\text{CO}_2$ . The total VOC amount at the outlet of the zero air generator is lower than 10 ppt. The second step allows  $\text{CO}_2$  to be removed from the air flow. At the outlet of the second step less than 10 ppbv of  $\text{CO}_2$  and 80 ppbv of  $\text{CO}$  are present in the gas stream. The obtained air flow is called zero-air, it was used to feed the experimental setup. A schematic diagram of the experimental setup is reported in Fig. 1.

### 2.1. VOC generator system

Toluene air stream at ppbv levels was supplied by a VOC generator system. First, liquid toluene is pressurized with helium in a stainless steel tank and a liquid flow is regulated downstream the tank using a Bronkhorst liquid mass flow regulator. Liquid toluene is heated, vaporized and mixed with a zero-air flow in an especially designed Bronkhorst vaporization/mixing chamber. The obtained gaseous air/toluene mixture is sampled and diluted twice in order to reach the targeted toluene concentration. Outlet toluene concentration is tunable from 1 ppbv to 1000 ppbv, with an accuracy of 20%. Downstream the VOC generator the gas stream contains 10 ppmv of  $\text{H}_2\text{O}$  corresponding to a relative humidity inferior to 0.01%. Humidity measurements were performed by Fourier Transform Infrared Spectrometry (FTIR) as described in Section 2.3. An additional gas line enabled the regulation of  $\text{H}_2\text{O}$  concentration at the outlet of the VOC generator to 15 500 ppmv; corresponding to a relative humidity of 50% at 25 °C. In order to investigate the influence of water vapor, reactions were performed in the presence of (i) 10 ppmv of water, so-called dry conditions, and (ii) 15 500 ppmv of water, so-called wet conditions.

### 2.2. Exposition chamber

Experiments were performed in a 120 L batch Pyrex reactor. The exposition chamber could be kept in the dark or illuminated by nine PL-L-40 Philips UV lamps characterized by a broad emission band centered at 365 nm. The photon flux was regularly measured using a SolaCheck photoradiometer in 70 different points of the exposition chamber. It evidenced that the photon flux was homogeneous in the chamber with an average of  $10 \pm 1 \text{ mW/cm}^2$ . Before each

**Table 1**  
TD-GC analytical parameters under dry air conditions.

TDS parameters	Initial temperatures (°C)	10
	Temperature ramp (°C min <sup>-1</sup> )	50
	Final temperature (°C)	250
	Final time (min)	10
	Flow rate (mL min <sup>-1</sup> )	50
Refocusing on CIS and Injection in GC	Initial temperature (°C)	-100
	Temperature ramp (°C s <sup>-1</sup> )	12
	Final temperature (°C)	250
Elution in chromatographic column	Final time (min)	10
	Initial temperature (°C)	0
	Initial time (min)	4
	Temperature ramp (°C min <sup>-1</sup> )	15
	Final temperature (°C)	250
	Flow rate (mL min <sup>-1</sup> )	4

experiment the chamber was preliminarily swept with humidified zero-air during a minimum of 12 h under UV irradiation in order to ensure the chamber and the photocatalyst cleaning. The photocatalyst used during the experiments consists in 100 mg of P25-Degussa TiO<sub>2</sub>. The powder was dispersed on the lower part of the reaction chamber. The reactor was swept in the dark with the VOC generator flow containing the targeted concentration of toluene during 14 h in order to reach the adsorption equilibrium in the chamber. Finally, the exposition chamber was closed and toluene concentration was monitored twice. Static experiments performed in the dark during 48 h have shown that once the chamber was closed, toluene decrease, due to leaks, is inferior to 5% over 24 h. During photocatalytic experiments,  $t=0$  was defined by the beginning of UV irradiation. Toluene concentration was monitored after 30 min of irradiation. Then, it was regularly monitored during illumination.

### 2.3. Analytical devices

In order to determine toluene and reaction intermediates temporal profiles, a maximum of 10 analyses of the chamber gas mixture were performed during the experiments. For each analysis, 1000 mL of gas was sampled from the chamber by the Thermodesorption System (TDS) Gerstel with a flow rate of 100 mL min<sup>-1</sup>. The sample was focused on a multi-bed cartridge (Carbosieve SIII, Carbopack B, Carbopack C). After heating, it was refocused on a trap filled with Carbopack B and cooled with liquid nitrogen, so-called Cooled Injection System (CIS). Injection was conducted splitless in an Agilent Gas Chromatograph (GC). The GC was equipped with an Agilent DB-5MS chromatographic column (60 m × 0.32 mm × 1 μm). This column was connected to two detectors: a Flame Ionisation Detector (FID) dedicated to compound quantification, and an Agilent Mass Spectrometer (MS) devoted to compound identification. Dry air corresponding analytical parameters are listed in Table 1. For wet air experiments (15 500 ppmv H<sub>2</sub>O), a multi-bed cartridge composed of three hydrophobic sorbents (Carbopack X, Carbopack B, Carbopack C) was used in order to prevent water trapping [19,20]. Likewise, the sampling temperature was set to 15 °C for these experiments. The oven temperature was set to 0 °C during the first 4 min of the elution. Then, it was

heated at 15 °C min<sup>-1</sup> up to 250 °C maintained during 5 min. The developed analytical methods enabled detection limits lower than 100 ppt for all compounds under dry and wet conditions. The calibration of the various compounds was preliminarily performed by loading the sampling cartridges with a known amount of compounds. These compounds were obtained either from the dilution of a gaseous mixture from certified gas cylinders supplied by Praxair, or from the vaporization of a liquid VOC mixture in a gas chromatograph oven. Identification of the compounds has been made using the mass spectrometer spectra and the NIST library. The detection limits of each compound identified in the gas phase during the photocatalytic degradation of toluene are reported in Table 2.

The gas chromatographic technique described above did not enable the detection of formaldehyde whereas this compound is expected to be one of the most abundant toxic by-product of photocatalytic VOC oxidation [13]. Thus, 1000 mL of the reaction chamber gas mixture was sampled in parallel using 2,4-dinitrophenylhydrazine (DNPH) Waters cartridges in order to perform carbonyl derivatization [21]. Those cartridges were eluted and analyzed by high-performance liquid chromatography (HPLC/UV). This analytical method permits the detection and the quantification of low molecular weight carbonyls. Details about this analytical method have been already exposed by Coddeville et al. [22]. The detection limit obtained on formaldehyde with this method is 10 ppb. Quantification of acetaldehyde performed by derivatization and using the GC analytical method lead to acetaldehyde quantifications differing by only 15%.

The detection and quantification of CO and CO<sub>2</sub> was performed using Thermo-Electron high resolution Fourier Transform Infrared Spectrometer (FTIR) Antaris IGS equipped with a heated 10 m optical-path cell and MCT (Mercury Cadmium Telluride) detector. The level of CO<sub>2</sub> in ambient air usually ranges from 350 to 400 ppmv. This level is much higher than the expected formation of CO<sub>2</sub> due to the photocatalytic mineralization of toluene. The highest concentration of toluene in the experiment is 800 ppbv. If we assume that toluene mineralization can be achieved, the highest expected CO<sub>2</sub> concentration in the reaction chamber would remain below 6 ppmv. This value is dramatically small in comparison to ambient air CO<sub>2</sub> concentration. Thus, the PSA system used to remove CO<sub>2</sub> from supplied air was necessary. The CO<sub>2</sub> free zero-air stream (less than 10 ppbv) was simultaneously used to feed the VOC generator and to purge the FTIR optical device.

FTIR spectra were collected using Result-3 software with 6 scans per spectrum and a spectral resolution of 0.5 cm<sup>-1</sup>. The fundamental asymmetric stretch vibration of CO<sub>2</sub> in the region 2388–2383 cm<sup>-1</sup> was selected for quantification. To avoid the overlapping region of absorption signals for CO and H<sub>2</sub>O, the quantification of CO is carried out using the average of four rotational absorption peaks associated to the C–O stretch vibration. The R(4), R(5), R(6) and R(7) peaks respectively 2163.5–2160.1 cm<sup>-1</sup>, 2167.4–2163.7 cm<sup>-1</sup>, 2170.7–2167.1 cm<sup>-1</sup>, 2173.1–2171.9 cm<sup>-1</sup> were selected. Calibration curves for CO and CO<sub>2</sub> were determined from passing through the gas-cell 1 L min<sup>-1</sup> of standard gases pro-

**Table 2**  
List of the reaction intermediates identified in the gas phase during toluene photocatalytic degradations. For each compound: “ $t_{\text{MAX}}$ ” corresponds to the temporal position of the maximum concentration during the photocatalytic degradation of 800 ppbv of toluene; “D.L.” indicates the detection limit of the compound using the GC analytical method.

Aromatics	$t_{\text{MAX}}$ (h)	D.L. (ppt)	Ketones	$t_{\text{MAX}}$ (h)	D.L. (ppt)	Aldehydes	$t_{\text{MAX}}$ (h)	D.L. (ppt)	Others	$t_{\text{MAX}}$ (h)	D.L. (ppt)
Benzene	∅	3	Acetone	>12	15	Formaldehyde	>14		2-methylfuran	1.5	5
Phenol	∅	7	Butanone	8	12	Acetaldehyde	>14	43			
Benzaldehyde	1.5	5	M.V.K.	2.5	12	Acroleine	4	29			
o-cresol	1.5	5				Propanal	∅	35			
m+p-cresol	1.5	6				Pentanal	2.5	9			
						Heptanal	2.5	7			

vided by Praxair. Calibration concentrations were adjusted from 240 ppbv to 10 ppmv. 500 scans were taken per standard spectrum. For calibration curves and quantifications data processing TQ-Analyst-8 software was used. The detection limits was evaluated as two times the Signal/Noise ratio in the region of interest and are, respectively, 10 ppbv and 76 ppbv for CO<sub>2</sub> and CO.

### 3. Results and discussion

#### 3.1. Toluene removal

The preparation of the reaction chamber requires 14 h in order to reach the adsorption equilibrium. This means that a steady state can be reached regarding the partition of toluene in the gas phase and in the adsorbed phase. During the experiments, measurements of organic compounds were only performed in the gas phase, whereas a fraction of toluene molecules is present at the beginning of the reaction on the photocatalyst surface. Those adsorbed molecules are supposed to react rapidly at the beginning of UV illumination and will take part to the carbon balance of the photocatalytic reaction regarding organic intermediate and CO<sub>2</sub> formation. The question is to determine the portion of toluene initially adsorbed on the photocatalyst in order to evaluate its potential contribution into the carbon balance. Demeestere et al. [23] have precisely investigated the equilibrium partitioning of various VOC on P25-Degussa TiO<sub>2</sub> surface, and determined toluene adsorption constant as a function of temperature, concentration and relative humidity. At 298 K, in the presence of 400 ppbv of toluene in our reaction chamber, corresponding to  $1.8 \times 10^{18}$  molecules in the gas phase,  $3.2 \times 10^{14}$  toluene molecules are adsorbed on the photocatalyst under dry conditions (10 ppmv H<sub>2</sub>O) and  $1.15 \times 10^{14}$  toluene molecules are adsorbed under wet conditions (15 500 ppmv H<sub>2</sub>O). Thus, the ratios between toluene amount in the gas phase and the adsorbed phase are around 3600 and 10 000 respectively under dry and wet conditions. Obee and Brown [24] suggest that toluene mainly adsorbs on TiO<sub>2</sub> surface hydroxyl groups. Thus, based on Mills and Le Hunte [25] considerations on TiO<sub>2</sub> active/adsorption sites it is possible to deduce the number of sites on the photocatalyst from: the OH surface density, the Brunauer–Emmet–Teller (BET) specific surface, and the mass of photocatalyst. In the presence of 100 mg of P25-Degussa TiO<sub>2</sub> we assume that the number of active/adsorption sites is superior to  $5 \times 10^{16}$ . This implies that at  $t=0$ , less than 0.64% and 0.23% of TiO<sub>2</sub> sites are supposed to be occupied by toluene, respectively, in the dry and wet conditions. The ratios of toluene amounts between the gas and the adsorbed phase and TiO<sub>2</sub> surface coverage suggest that (i) the initial adsorbed toluene molecules are not significant in the photocatalytic reaction carbon balance; (ii) no induction period due to adsorbed toluene removal can be expected at the beginning of the photocatalytic reactions.

The photocatalytic oxidation of toluene was carried out for various initial concentrations ranging from 50 to 800 ppbv under dry and wet conditions. Decay profiles of toluene observed under dry air are reported in Fig. 2 as a function of irradiation time. Standard deviations associated to the experimental data reported in Fig. 2 have not been plotted in order to make the reading of the graph easier.

In order to investigate the experiment reproducibility, the photocatalytic removal of 800 ppbv of toluene was successively investigated 5 times during 20 h without any regeneration procedure between the degradations; the obtained removal profiles were characterized by a standard deviation lower than 10 ppb. The fact that toluene removal can be performed with such reproducibility indicates that no by-product compounds irreversibly poisoned the photocatalyst surface. Nevertheless, the photocatalyst regen-

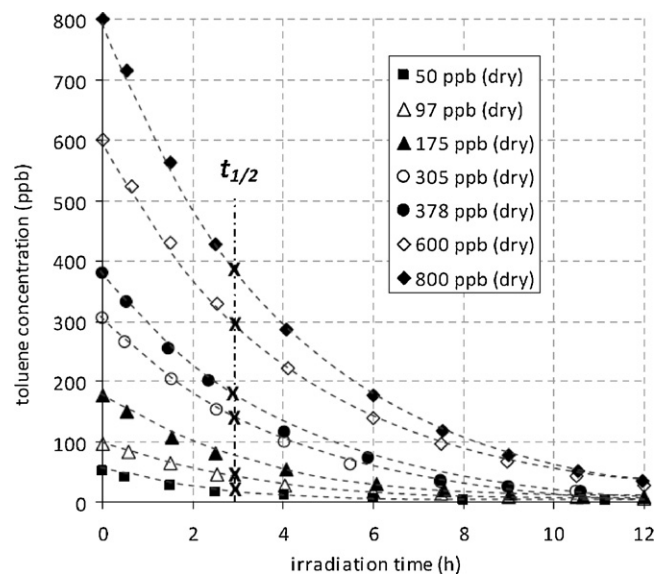


Fig. 2. Evolution of toluene concentration as a function of irradiation time during the photocatalytic oxidation of toluene under dry air (10 ppm H<sub>2</sub>O).

eration procedure has been performed between degradations to ensure long term experiment reproducibility.

The graphical determination of the half reaction time ( $t_{1/2}$ ) under dry air for each reaction (Fig. 2) indicates that this parameter does not depend on toluene initial concentration on the investigated concentration range. This point was noticed for both dry and wet series of experiments. Values of  $t_{1/2}$  are 3.0 h and 2.7 h, respectively during dry and wet air toluene removal. The fact that  $t_{1/2}$  does not depend on reactant initial concentrations suggests that toluene photocatalytic removal at ppbv level is a pseudo-first-order reaction. Toluene reaction rate  $r$  can be expressed by the following equation (Eq. (1)), where  $k$  represents the reaction constant,  $[To]$  represents the concentration of toluene and  $n$  the reaction order.

$$r = k \cdot [To]^n \quad (1)$$

Fig. 3 reports the evolution of  $\ln(r)$  as a function of  $\ln([To])$  during photocatalytic reactions performed under dry (a) and wet (b) air for various toluene initial concentrations. Linear evolutions can be noticed in Fig. 3 under both conditions for each reaction. This linear behaviour enables the determination of the reaction order ( $n$ ) and the reaction constant ( $k$ ) for each photocatalytic reaction. Data obtained on same series of experiments (dry or wet) are characterized by a low dispersion. Therefore, average values were calculated for each condition. Average values of  $n$  are equivalent under dry and wet air, respectively,  $1.07 \pm 0.06$  and  $1.03 \pm 0.08$ , confirming for both series of experiments a pseudo-first-order reaction. On the contrary, reaction rate values appear to be slightly influenced by the presence of water vapour:  $0.19 \pm 0.03 \text{ h}^{-1}$  and  $0.22 \pm 0.02 \text{ h}^{-1}$  respectively under dry and wet air. In the presence of humidity, the slight increase of  $k$  is coherent with the decrease of  $t_{1/2}$ , suggesting an enhancement of the photocatalytic reactivity due to the formation of HO<sup>•</sup> radicals. Nevertheless, the positive influence of water vapour on toluene disappearance is weak in comparison to the dispersion of the experimental data, which makes difficult the precise quantification of the enhancement through toluene reaction rates.

#### 3.2. Gas phase reaction intermediates

Simultaneously to toluene removal monitoring, reaction intermediates formation and removal were monitored with appropriate analytical procedures. During toluene photocatalytic degradation, 15 VOC were evidenced in the reaction chamber gas phase. Com-



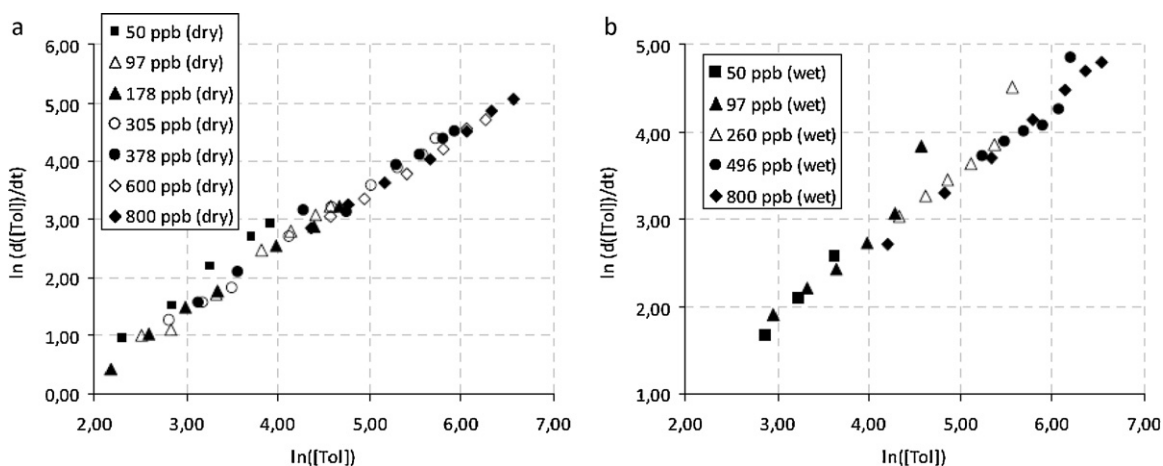


Fig. 3. Evolution of  $-\ln(d[\text{Tol}]/dt)$  as a function of  $\ln[\text{Tol}]$ : (a) under dry air (10 ppm H<sub>2</sub>O), (b) under wet air (13 000 ppm H<sub>2</sub>O).

pounds are listed in Table 2 and classified according to their chemical natures. The same reaction intermediate diversity was found for each reaction, independently of the initial concentration. Among the identified reaction intermediates, 12 of them were quantified. The evolution of their concentration is reported as a function of irradiation time in Fig. 4. Traces of benzene, phenol and propanal have been identified, but reliable quantification has not been performed for these compounds because of the weakness of their signals.

VOC profiles reported in Fig. 4(a–c) are characterized by (i) a formation period, (ii) a maximum concentration, (iii) a removal period. The temporal position of the maximum is listed in Table 2 for each reaction intermediate. Benzaldehyde, o-, m-, and p-cresols are

characterized by the shortest maximum temporal positions, thus, they can be considered as toluene primary reaction intermediates in the gas phase. Indeed, Coronado and Soria [26] reported that toluene reaction onto TiO<sub>2</sub> leads to the formation of benzyl radical and subsequently, in the presence of O<sub>2</sub>, to the formation of peroxybenzyl radicals. Then, benzaldehyde is formed and a HO• radical is released. Besides, cresols are produced by the direct attack of HO• radicals on the aromatic ring. Even if benzaldehyde appears as a key point into toluene photocatalyst oxidation pathway, the highest concentration of benzaldehyde in the gas phase does not exceed 3.5 ppbv. Two reasons can explain this phenomenon: (i) benzaldehyde is strongly adsorbed on TiO<sub>2</sub> surface (benzaldehyde desorption activation energy:  $E_d = 121\text{--}124$  kJ/mol) [27]; (ii) ben-

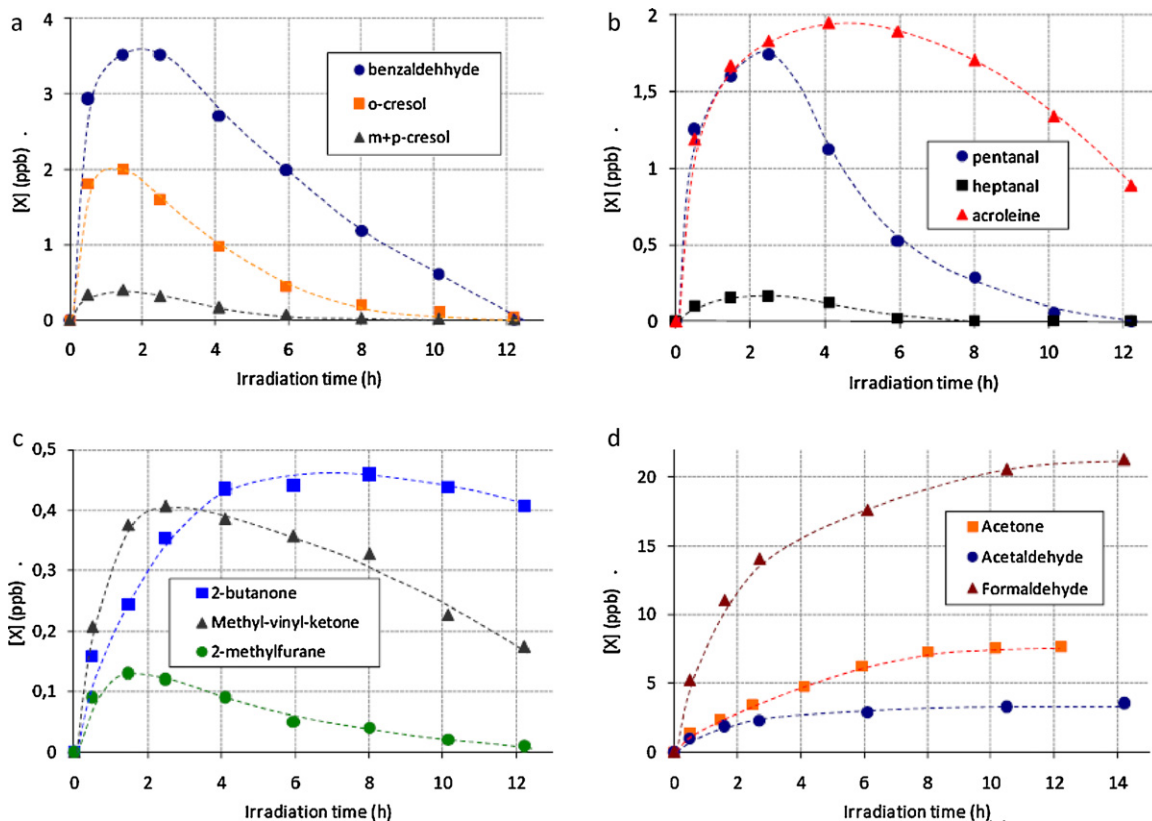


Fig. 4. Evolution of the 12 major reaction intermediate concentrations as a function of irradiation time during the photocatalytic degradation of 800 ppb of toluene under wet conditions (13 000 ppm H<sub>2</sub>O).

zaldehyde is rapidly oxidized into benzoic acid in the adsorbed phase by hydroxyl groups [28]. During the conducted experiments, no benzoic acid was detected in the gas phase. This compound, condensed at room temperature, accumulates on photocatalyst surface. Similarly, Marci et al. [29] reported the presence of benzoic acid as reaction intermediate during toluene photocatalytic oxidation only in the adsorbed phase. However, this compound is sensitive to photocatalytic oxidation. For instance, benzene, identified as traces in the reaction chamber, can be produced from photo-Kolbe reaction on benzoic acid, leading to the simultaneous formation of  $\text{CO}_2$  [10,16].

Secondary reaction intermediate temporal evolutions are reported in Fig. 4(b–d). Their non-cyclic structures indicate that they originate from aromatic ring-opening reactions. Aldehydes are the major compounds in terms of diversity and concentration in the gas phase. Nevertheless, the presence of 2-methylfuran suggests recombination phenomena occurred in a minor way. The concentration decrease of compounds containing more than 4 carbon atoms is noticeable within the 12 h of illumination. However, lighter reaction intermediates (acetone, acetaldehyde, formaldehyde) are characterized by stable concentrations after 10 h of irradiation. Formaldehyde can be considered as the main gaseous reaction intermediate regarding concentration. This step of toluene photocatalytic oxidation pathway is rarely investigated in details by authors since it leads to the formation of numerous and various aliphatic compounds which are generally considered as sensitive to photocatalytic oxidation. Under our conditions, it appears that lighter compounds are not removed from the gas phase within 12 h experiments. One hypothesis is that adsorbed reaction intermediates accumulated on the photocatalyst surface are slowly oxidized into acetone, acetaldehyde and formaldehyde several hours after toluene and gaseous reaction intermediates removal. This hypothesis could be confirmed through the investigation of CO and  $\text{CO}_2$  formation. The formation of CO and/or  $\text{CO}_2$  after 14 h of irradiation would be an evidence for adsorbed reaction intermediates photocatalytic oxidation. Moreover these light and volatile compounds are generally characterized by low heat of adsorption in comparison to longer aliphatic chain compounds. Thus short carbonyl would adsorb onto  $\text{TiO}_2$  once heavier compound have been oxidized. The removal kinetic of these compounds would decrease. This hypothesis could be confirmed investigating and comparing the degradation kinetic of compounds characterized by various heat of adsorption, first individually, then, in a mixture.

### 3.3. CO and $\text{CO}_2$ formations: mineralization

Toluene mineralization at ppbv level was investigated through  $\text{CO}_2$  and CO formation. Measurements were performed with 800 ppbv of toluene as initial concentration under dry (10 ppm  $\text{H}_2\text{O}$ ) and wet (15 500 ppmv  $\text{H}_2\text{O}$ ) air.

The evolution of  $\text{CO}_2$  concentration during the photocatalytic process is reported in Fig. 5. Under both humidity conditions, the formation of  $\text{CO}_2$  starts since the beginning of UV irradiation. This means that  $\text{CO}_2$  is produced from the initial pollutant first oxidation steps, suggesting that the oxidation, and abstraction, of toluene methyl groups can lead to the formation of  $\text{CO}_2$ . In the presence of 15 500 ppmv water vapor,  $\text{CO}_2$  concentration is 60% higher than under dry conditions during the whole photocatalytic process. It clearly highlights the positive role of  $\text{H}_2\text{O}$ , and subsequently  $\text{HO}^\bullet$  radicals, on the oxidation reaction advancement. The influence of  $\text{H}_2\text{O}$  on the oxidative processes is more noticeable on the mineralization than on toluene removal. This phenomenon has been formerly observed by Blount and Falconer [10] and Fu et al. [30] with higher toluene initial concentrations. Thus, even at ppbv levels, the addition of water does not significantly improve toluene consumption, but considerably increases the mineraliza-

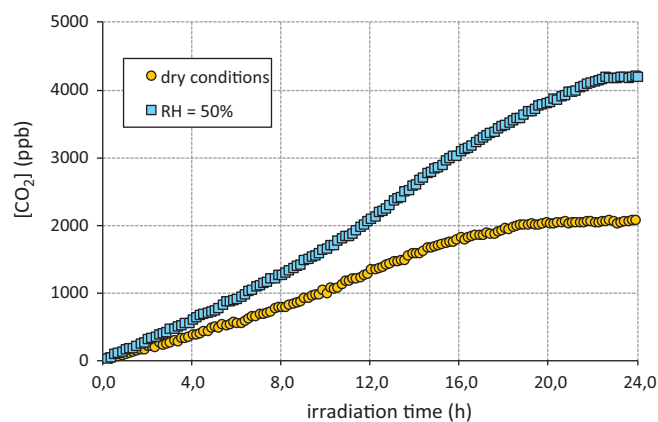


Fig. 5. Evolution of  $\text{CO}_2$  concentration during the photocatalytic oxidation of 800 ppbv of toluene under dry (10 ppm  $\text{H}_2\text{O}$ ) and wet (13 000 ppm  $\text{H}_2\text{O}$ ) air as a function of irradiation time.

tion of intermediates to  $\text{CO}_2$ . The formation of  $\text{CO}_2$  gets stabilized only after 19 h and 22 h illumination respectively under dry and wet conditions. This indicates that significant amounts of organic compounds are mineralized after toluene removal from the gas phase (10–14 h). Thus, the hypothesis of reaction intermediates accumulated onto  $\text{TiO}_2$  leading to the formation of acetone, acetaldehyde, formaldehyde and  $\text{CO}_2$  is confirmed. Most part of the reaction pathway would take place in the adsorbed phase. The temporal profiles of  $\text{CO}_2$  concentration are characterized by a sigmoid shape, indicating that  $\text{CO}_2$  formation rates vary during the reaction. In order to investigate the temporal evolution of  $\text{CO}_2$  formation rates, data from Fig. 5 have been interpolated using a fourth order polynomial equation.  $\text{CO}_2$  formation rates have been deduced from the derivation of the obtained expression. The evolution of  $d[\text{CO}_2]/dt$  is reported as a function of irradiation time in Fig. 6.

As reported in Fig. 6,  $\text{CO}_2$  formation rates under wet conditions exceeds by around 60% formation rates calculated in the absence of humidity. This phenomenon is noticeable during the whole photocatalytic reaction. Nevertheless, temporal profiles of  $\text{CO}_2$  formation rates are similar under dry and wet air. The variations of  $\text{CO}_2$  formation rates can be correlated to the evolution of the main reaction intermediate nature. From 0 to 4 h,  $\text{CO}_2$  formation rates are constant, toluene is still abundant in the reaction chamber and main reaction intermediates are aromatic compounds. Those species are characterized by high heats of adsorption and good stability on  $\text{TiO}_2$  surface (benzaldehyde, benzoic acid). Under our conditions, ppbv levels of initial pollutant do not lead to deactivation, but to

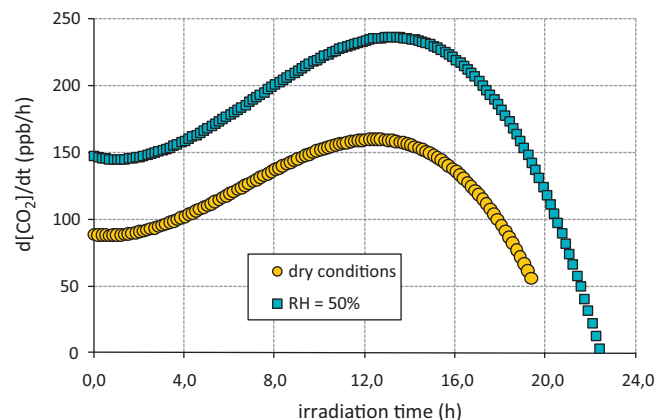
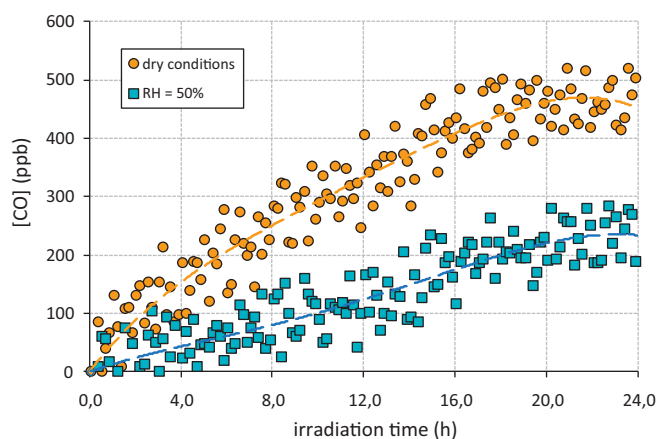


Fig. 6. Evolution of  $\text{CO}_2$  formation rate during the photocatalytic oxidation of 800 ppbv of toluene under dry (10 ppm  $\text{H}_2\text{O}$ ) and wet (13 000 ppm  $\text{H}_2\text{O}$ ) air as a function of time.



**Fig. 7.** Evolution of CO concentration during photocatalytic oxidation of 800 ppb of toluene under dry (10 ppm H<sub>2</sub>O) and wet (13 000 ppm H<sub>2</sub>O) air as a function of irradiation time.

low mineralization during the first 4 h of reaction. Even if water vapor improves CO<sub>2</sub> formation rate values, the same phenomenon is observed under wet conditions.

After 4 h, the main reaction intermediates in the chamber are issued from ring opening of aromatic compounds. Comparing the conversion rates of 17 different VOCs under the same experimental conditions, Alberici and Jardim [31] have shown that conversion rates of aromatic compounds were among the lowest. Linear, oxidized and lighter compounds lead to the best conversion rates. Thus the increase of CO<sub>2</sub> formation rates after 4 h of irradiation can be explained by the evolution of the gas phase composition. Mineralization is improved once major reaction intermediates are linear and oxidized. The highest CO<sub>2</sub> formation rate is observed when short and oxygenated VOC like acetone, acetaldehyde and formaldehyde are the major reaction intermediates. Thus the mineralization process is directly linked to the nature of VOC to be oxidized.

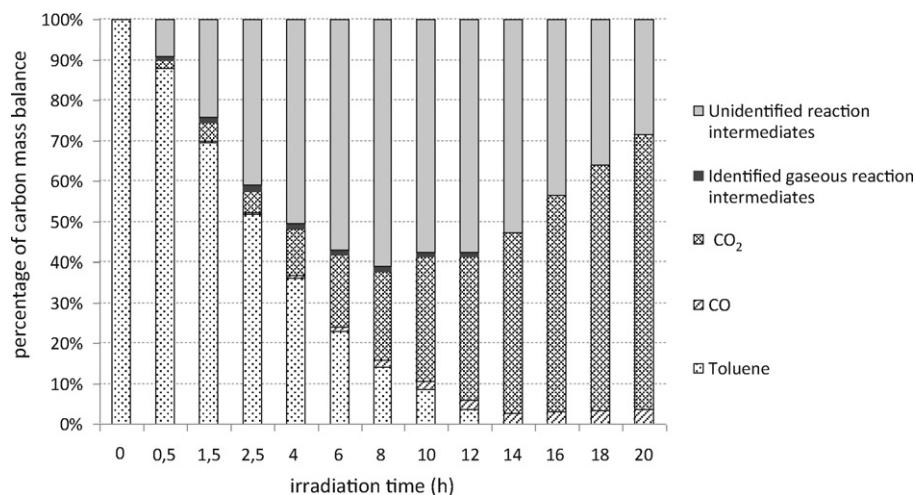
The evolution of CO concentration is reported in Fig. 7 under dry and wet conditions. Data dispersion is observed in Fig. 7 is due to the fact that CO detection limit is 70 ppbv. Nevertheless, it appears that CO amounts are significantly inferior (50%) in the presence of 15 500 ppmv water vapor. Two hypotheses can be made to explain this behaviour: (i) the presence of water vapor modifies the VOC oxidation pathway so that CO is less produced; (ii) the presence of water vapor improves CO oxidation into CO<sub>2</sub>. Since no modifica-

tion of VOC formation order and nature in the gas phase has been observed, the second hypothesis would be favored. Moreover, it confirms that H<sub>2</sub>O considerably improves the mineralization process toward CO<sub>2</sub> formation.

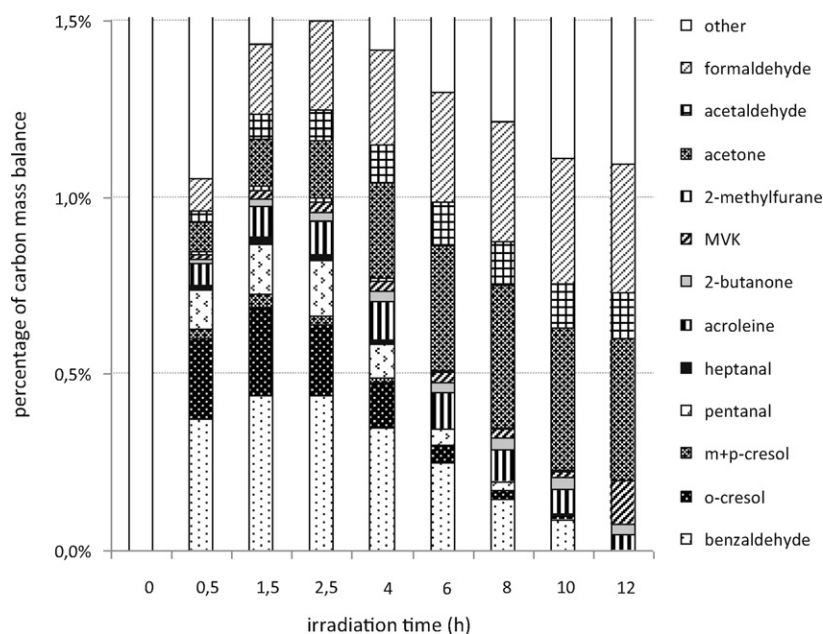
### 3.4. Carbon mass balance analysis

The simultaneous monitoring of toluene removal, reaction intermediates, and CO and CO<sub>2</sub> formation enables the calculation of carbon mass balances as a function of the oxidation reaction advancement. This was performed for a toluene initial concentration of 800 ppbv in the presence of 15 500 ppmv of water vapor. The presence of 800 ppbv of toluene in the reaction chamber is equivalent to 5600 ppbv of carbon. Considering that experiments performed in a static batch reactor are operated with a constant amount of carbon. The percentage represented, in the carbon balance, by (i) toluene, (ii) CO, (iii) CO<sub>2</sub>, and (iv) identified reaction intermediates are reported in Fig. 8 for various irradiation times. The contribution of identified reaction intermediates is reported in Fig. 8 only until 12 h of irradiation since measurements have not been performed further. The missing part of the carbon balance is reported in grey and labeled as 'unidentified reaction intermediates'.

Fig. 8 highlights the fact that in spite of a complete removal of toluene achieved within 12 h, mineralization of the pollutants mainly occurs after 12 h. The contribution of the gaseous organic compounds identified and quantified in the gas phase does not exceed 1.5% of the carbon balance, indicating that most part of the organic reaction intermediates remain unidentified. The contribution of the unidentified reaction intermediates exceeds 60% of the carbon balance after 8 h of irradiation. Regarding the analytical technique diversity and performances developed for the gas phase characterization, we suggest that most part of the unidentified reaction intermediates are adsorbed on the photocatalyst surface. Once toluene and aromatic reaction intermediates are removed from the chamber, the strong increase of CO<sub>2</sub> contribution in the carbon balance evidences the fact that adsorbed reaction intermediates do not permanently deactivate the surface. Those unidentified compounds can be mineralized if the irradiation time is sufficient and the composition of the gas phase appropriate. Nevertheless, in the case of a one pass continuous flow reactor, the constant feeding with toluene, even at ppbv level, could lead to (i) poor mineralization of the pollutant, (ii) possible lowering of the photocatalyst activity. We suggest that sequential regeneration phases of the photocatalyst under humid air are



**Fig. 8.** Contribution of toluene, CO, CO<sub>2</sub>, identified gaseous reaction intermediates and unidentified reaction intermediates into the carbon mass balance of 800 ppb toluene photocatalytic degradation in the presence of 13 000 ppm H<sub>2</sub>O, for various irradiation times.



**Fig. 9.** Contribution of the identified gaseous organic reaction intermediates to the reaction carbon mass balance during the photocatalytic degradation of 800 ppb of toluene in the presence of 13 000 ppm H<sub>2</sub>O, for various irradiation times.

required to ensure surface cleaning even under indoor air treatment conditions.

The contribution of the identified gaseous reaction intermediates into the carbon balance ranges from 1 to 1.5% until 12 h of irradiation. The fact that a low percentage of the carbon balance is released in the gas phase during the photocatalytic process is a positive point regarding air treatment in that the emission of reaction intermediates is limited. Fig. 9 evidences the evolution of reaction intermediate diversity as a function of the oxidation reaction advancement. During the reaction first two hours, aromatic compounds represent from 60 to 75% of the gaseous reaction intermediate carbon mass balance. After 10 h of reaction, more than 80% of the gaseous reaction intermediate carbon mass balance is made of aliphatic oxidized VOC containing less than 4 carbon atoms. The low concentration of reaction intermediates in the gas phase during the oxidation process can be balanced by the toxicity of the considered compounds. For instance, formaldehyde has to be carefully examined in the frame of air treatment devices qualification. After 12 h of batch treatment, formaldehyde, acetone and acetaldehyde represent more than 80% of the gas phase reaction intermediate carbon mass balance (Fig. 9).

#### 4. Conclusion

In this paper, a complete characterization of gas phase species present during toluene photocatalytic removal was presented. This approach combined for the first time, the kinetic characterization of toluene as initial pollutant with the monitoring of reaction intermediates, CO and CO<sub>2</sub> at ppbv levels. In order to make reaction condition closer to indoor air atmosphere, toluene initial concentration were ranging from 50 to 800 ppbv and the influence of water vapour was investigated. The development of appropriate analytical techniques like ATD–GC–FID–MS and FTIR direct spectroscopy enabled the determination of precise carbon mass balance based on gas phase species.

The results showed that toluene removal can be efficiently achieved at ppbv levels. The disappearance of the compound is slightly influenced by the presence of 50% relative humidity. Toluene photocatalytic oxidation follows a pseudo first order

kinetic on the investigated concentration range. Carbon mass balance calculations based on the quantified reaction intermediates evidenced that their abundance in the carbon balance is limited (less than 1.5%), but remains constant along the oxidation reaction. Once toluene is removed from the gas phase the major reaction intermediates are acetone, acetaldehyde and formaldehyde. Those compounds are not removed from the gas phase within 14 h irradiation. Subsequently attention has to be paid to acetone, acetaldehyde and formaldehyde regarding the efficiency of air treatment devices and indoor air quality. The challenge of monitoring of CO and CO<sub>2</sub> produced by the photocatalytic reaction gives interesting information. Firstly, we evidenced that CO<sub>2</sub> formation rate was increased by 60% in the presence of 50% relative humidity. Secondly, the formation of CO<sub>2</sub> and CO lasts several hours after the disappearance of toluene from the gas phase. This observation suggests that the most part of the reaction intermediates remained unidentified and were adsorbed on the photocatalyst.

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