



## Determination and risk assessment of by-products resulting from photocatalytic oxidation of toluene

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### ABSTRACT

The generation of harmful by-products during photocatalytic oxidation (PCO) of volatile organic compounds (VOCs) is a bottleneck problem for the application of PCO technology in indoor environment. Toluene is a typical VOC found in indoor air. In this work, the by-products at ppb level were studied during PCO decomposition of toluene in a plate-type reactor and identified using PTR-MS (proton transfer reaction-mass spectrometry) and GC-MS (gas chromatography-mass spectrometry). The results indicated that benzaldehyde, methanol, acetaldehyde, acetone/propionaldehyde, formic acid/ethanol and acetic acid were the main by-products in the gas phase. By adjusting the concentration of water vapor, some compounds adsorbed on the TiO<sub>2</sub> surface were ascertained, which resulted in the deactivation of TiO<sub>2</sub>. They were benzoic acid, benzene, acrylaldehyde, butyraldehyde and pentanal. Some of these by-products have not been reported in the literature. Possible photocatalytic oxidation pathways of toluene were proposed. A health-related index (HRI) was introduced to assess the risk level to human health of these ppb-level by-products. It concludes that although some undesired by-products (even carcinogenic) are generated during PCO decomposition of toluene, it seems that these by-products do not have negative effects to human health because of their low concentrations.

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## 1. Introduction

Indoor materials and products tend to emit volatile organic compounds (VOCs), such as toluene, benzene, formaldehyde [1]. They have been found to be associated with asthma, nasopharyngeal cancer and multiple subjective health complaints [2]. Photocatalytic oxidation (PCO) is an innovative and promising approach to eliminating VOCs indoors [3]. The resultant of complete PCO for VOCs should be CO<sub>2</sub> and water. However, some reactants will generate partial oxidation products [4–6], which are relatively more harmful to people's health. It inhibits the application of PCO technology in indoor environment. More study of by-products from PCO decomposition of VOCs should be performed.

Toluene, as one of the typical organic compounds indoors, was used as the target pollution species in this study. Although, many studies have investigated the PCO of gas-phase toluene by using TiO<sub>2</sub>, most of them focused on PCO rates and PCO reactor performance rather than on the identification of by-products

[7–12]. Gas chromatograph-flame ionization detector (GC-FID), GC-MS (gas chromatography-mass spectrometry), high performance liquid chromatography (HPLC), Fourier-transform infrared spectroscopy (FTIR), temperature-programmed oxidation (TPO) and temperature-programmed hydrogenation (TPH) are often used to characterize the by-products of toluene PCO [4–6,13–20]. It appears that no significant by-products of toluene were identified using GC-FID [13]. Combined with GC/FID/MS, GC/MS/HPLC, GC/FTIR or TPH and TPO, some by-products were found on the PCO reaction surface. These were primarily solid-phase products. The only gas-phase by-product found was CO. FTIR has been widely used to analyze the surface by-products of toluene. However it seems that FTIR is only suited to situations where the toluene concentration is high, from 30 to 13,000 ppm in the published articles [4,20–22]. Benzaldehyde, benzyl alcohol, benzoic acid and phenol were the main by-products [5,6,15,22]. Since the concentration of toluene in indoor air is ppb or sub-ppm levels, it is doubted whether the investigation conclusions from these high concentration experiments could be used to indoor air cases. In addition, here is also concern that there are gas-phase by-products as well as the solid-phase ones. There is, however, very little research concerning low concentration, gas-phase by-products reported in the literature. Sleiman et al. [23] found that

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benzaldehyde and benzene were the main gaseous by-products of toluene at indoor air levels. However, little discussion about the health effect of these by-products to human was included. Therefore, it is difficult to regard PCO as a reliable technique for decomposing indoor VOCs.

In order to determine the by-products resulting from the PCO of gas-phase toluene under indoor level and assess the risk level of applying such technique, we carried out experimental research on a plate-type PCO reactor. Since online PTR-MS (proton transfer reaction-mass spectrometry) has been proved to be a powerful device for online detecting transient by-products [24], we used PTR-MS to study PCO gas-phase by-products of a continuous flow of toluene over  $\text{TiO}_2$ . GC/MS was also used to identify part of the by-products by continuous extraction. The instant concentration pulse of water vapor was performed to replace the adsorbed by-products on  $\text{TiO}_2$  surface, which were released into gas phase and monitored by PTR-MS. Benzaldehyde, methanol, acetaldehyde, acetone/proprionaldehyde, formic acid/ethanol and acetic acid were found to be the main by-products, which were accompanied by benzoic acid, benzene, acrylaldehyde, butyraldehyde and pentanal. The possible PCO pathways of toluene were also analyzed. Finally, the risk assessment to human health of these by-products was discussed using a parameter, health-related index (HRI).

## 2. Experimental

### 2.1. UV-PCO reactor

A stainless steel plate-type UV-PCO reactor was used in this study (see Fig. 1). The experiments were all performed at a common indoor air conditioning level with temperature of 24.0–26.0 °C, and relative humidity (RH) of 47–50%. Two photocatalyst-coated glass plates (76.0 mm × 25.0 mm × 1.0 mm) were placed in the reactor. The photocatalyst powders (Degussa P25) were deposited on the glass plate as a film using the dip-coating method [9] with a net weight of 22 mg loading on the reaction side. Two UV-C lamps were used to irradiate the photocatalyst film from the top of the reactor through a quartz glass. The lamps (Philips Hg-Lamp, TUV 15 W G15T8 UV-C, made in Holland) with 98% of the UV lamp radiation emitted at 254 nm and the UV radiation

intensities were in the range of 0.43–0.95 mW/cm<sup>2</sup> on the reaction surface. The UV radiation intensity was measured by a UVC power meter (HANDY 00000176, made in China). Compressed air from a gas cylinder was divided into two streams. One stream passed through a mass flow controller and the other passed through a bottle-wash humidifier to control the humidity concentration. Pure toluene gas was mixed with the compressed air and then was supplied to the plant-type PCO reactor. All the air flow rates were controlled by two mass flow controllers. The total airflow rate was kept at 0.55 l/min with the contact time of 0.2 s in the reactor.

### 2.2. VOC concentration measurement

#### 2.2.1. PTR-MS analysis

A standard type of PTR-MS (Ionicon Analytik, made in Austria) was applied in the experiments, whose principle is based on proton-transfer reactions from  $\text{H}_3\text{O}^+$  ions to gaseous organic analytes with a higher proton affinity (PA) than water [24]. Water has a PA of 7.22 eV (166.5 kcal/mol). Molecules with PAs lower than 7.22 eV cannot be detected by PTR-MS. For most of the non-organic air-components, such as  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , they have lower PAs than water. However, most of the indoor organic compounds have higher PAs than water. PAs of common clean air and various VOCs were shown in Table A of the Supplementary Material (SM). Mass-scan and mass-identification-detection (MID) modes were used during the research. Mass-scans were performed in the mass-to-charge (m/e) range of 21–250 at a dwell time of 500 ms per m/e. MID was used to continuously trace some specific compounds found from the mass-scan mode. The temperatures of the detection chamber and the sampling tube were set to 60 °C.

#### 2.2.2. GC-MS analysis

The gas-phase by-products were concentrated from the outlet gas by an adsorption tube packed with Tenax TA. Due to the low concentration of by-products, the concentration process was performed to be over 10 h. Qualitative analysis filtrate was carried out using a GC-MS (Agilent 6850) with Automatic Thermal Desorption (ATD) system (Markes UNITY).

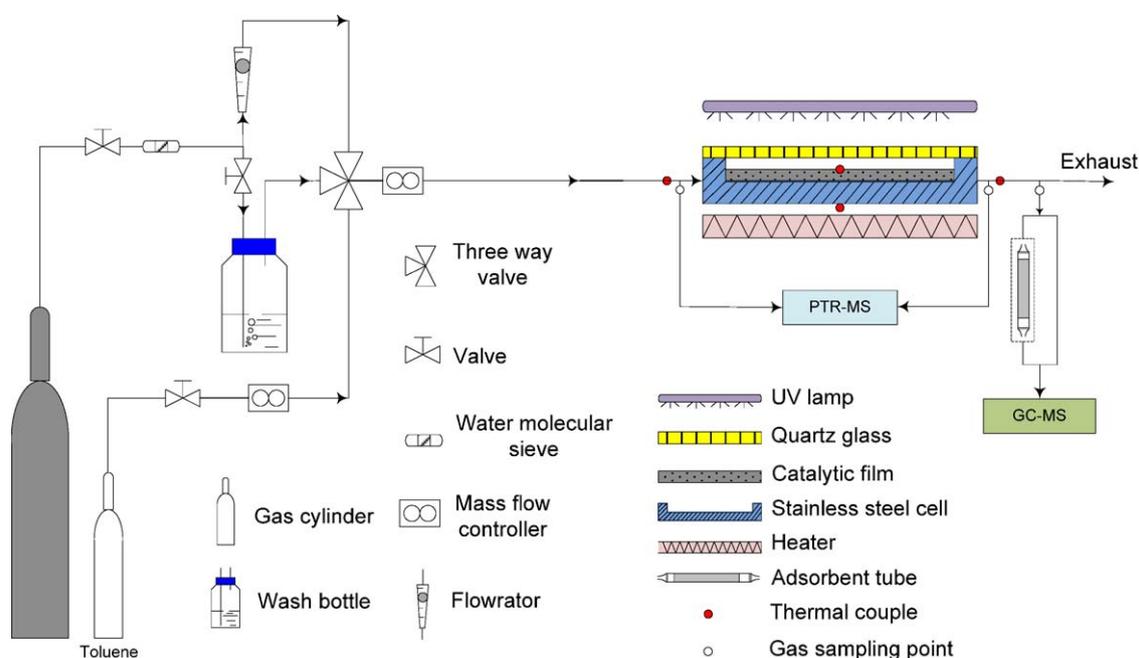


Fig. 1. Schematic of the experimental system, including the gas preparation part and UV-PCO reaction cell.

**Table 1**  
Experiment procedures to detect the intermediates of toluene PCO.

No.	Procedures	Description
1	Gas preparation	Adjust the mass flow controller, humidity concentrations.
Mass-scan (21–250 m/e)		
2	Inlet scan	Turn on the valve in the bypass channel and turn off the valves in the reactor channel (Fig. 1); full scale mass-scan in the range of 21–250 m/e.
3	Toluene scan	Adjust the inlet toluene concentration; full scale mass-scan.
4	Absorption checking	Turn off the valve in the bypass channel and turn on the ones in the reactor channel; scan the outlet compounds and check the absorption effect of the reactor to toluene.
5	UV on	Turn on UV lamps. Keep the mass-scan.
6	UV off	Turn off UV lamps. Check whether the outlet concentrations go back to the inlet levels.
Mass-identification-detection (MID)		
7	Suspected intermediates	Analyze the difference of intermediates from the blank glass and TiO <sub>2</sub> coated glass; identify the suspected intermediates of toluene PCO.
8	Repeat steps 2–5	Under the MID mode, repeat steps 2–6 and get the trace of the suspected intermediates identified by step 7.
Adsorption		
9	Adsorption	Apply adsorption tube packed with Tenax TA to concentrate the gas from outlet.
10	GC–MS analysis	Use GC–MS to identify the adsorbed compounds.

### 2.3. Procedure

The concentrations in the inlet air were adjusted to be 450, 1200 and 8000 ppb for toluene, while RH of 47–50% for water vapor. The blank glass without TiO<sub>2</sub> film and the TiO<sub>2</sub> coating glass was put into the PCO reactor, respectively. The by-products of toluene PCO were ascertained through real-time monitoring the outlet of PCO reactor in the cases with and without TiO<sub>2</sub> films. The detail of the experimental procedures was shown in Table 1. To ensure that no photoactivity decay occurred due to strongly adsorbed, oxidizable by-products, the glass with TiO<sub>2</sub> film was regenerated after each experiment by continuous illumination and flow of humid air through the reactor overnight. An instant water vapor pulse was also performed in order to detect the by-products adsorbed on the TiO<sub>2</sub> film. Water vapor was adjusted from 1.1% to 84% instantly with inlet toluene of 3200 ppb and UV intensity of 0.43 mW/cm<sup>2</sup>.

## 3. Results

### 3.1. By-products detected via PTR-MS

PTR-MS mass-scan mode was carried out with the initial toluene concentrations of 450, 1200 and 8000 ppb. In the experiments, the compounds with molecular mass 30, 32, 42, 44, 46, 58, 60, 78 and 106, were found to be the by-products. The concentrations of molecular mass 30, 32, 42, 44, 46, 58 and 60 always increased after UV irradiation. The concentrations of molecular mass 78 and 106 were only found to increase when the inlet toluene concentrations are 1200 and 8000 ppb. The by-products with molecular mass 30, 32, 42, 44 and 58 have not previously been reported in the literature.

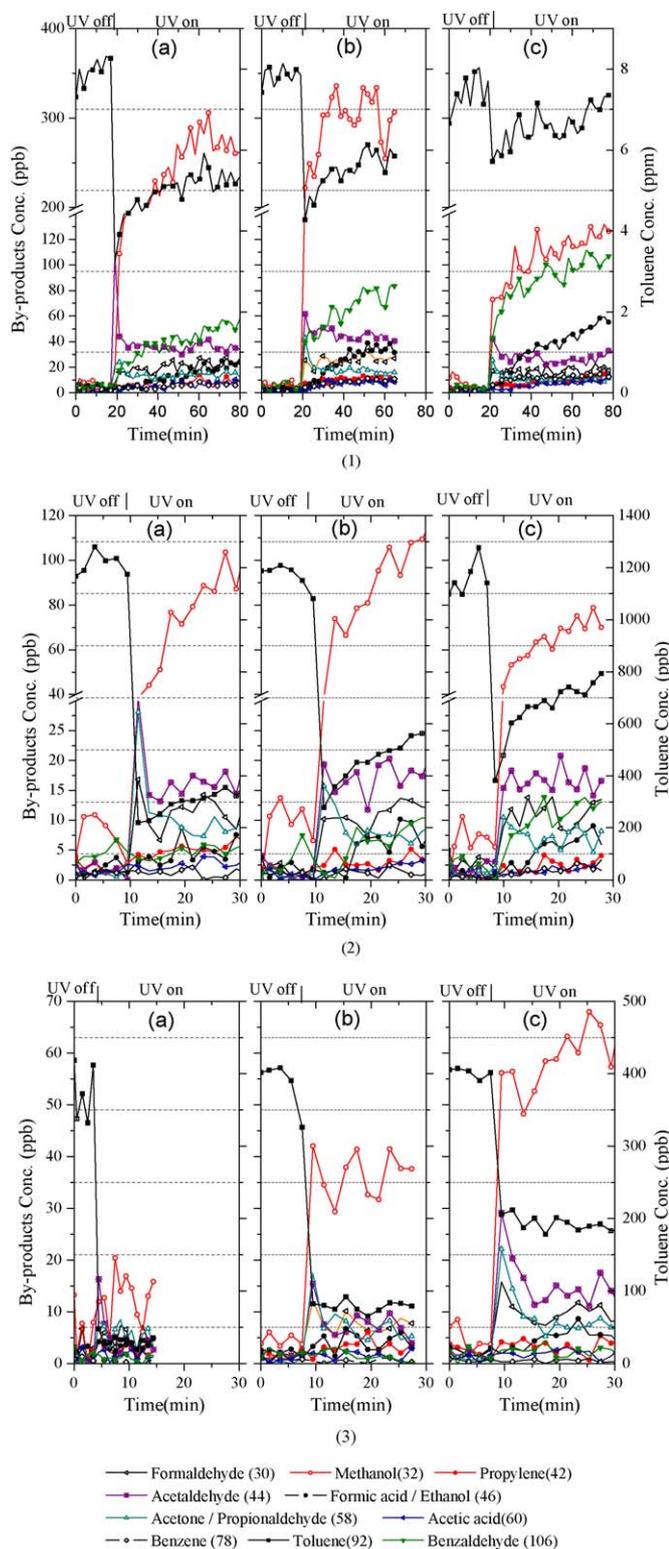
In order to observe the instant changes of by-products, the compounds identified in the mass-scan process were traced continually in MID process. No adsorption effect of molecular mass 30, 32, 42, 44, 58, 60, 78 and 106 on the interior surface of reactor cell was observed before and after the UV light irradiated on the blank glass without TiO<sub>2</sub> film. Fig. 2 shows the conversions versus time before and after UV light irradiated on the glass with TiO<sub>2</sub> film at different inlet concentrations and UV intensities. Under the experimental condition, the concentrations of molecular mass 44 and 58 increased sharply at the beginning of UV-PCO reaction (UV on) and trended to be steady state. The concentration peaks of molecular mass 44 and 58 were much high under high inlet toluene levels and high UV intensity (Fig. 2(1-a) and (2-a)). Simultaneously, the compounds with molecular mass 32, 46 and 106 were generated but the increases were slower compared with

the compounds of molecular mass 44 and 58. Molecular mass 78 was only found to have slight and regular change when the inlet concentration of toluene was 8000 ppb (Fig. 2(1)).

Under the instant concentration pulse of water vapor, the by-products adsorbed on TiO<sub>2</sub> surface were replaced by water vapor due to their completed adsorption effect. These by-products were released into gas phase. Fig. 3 shows the concentration changes of the by-products. Under UV irradiation and lack of water vapor (RH: 1.1%), the inlet and outlet concentrations of toluene were almost the same. It means that PCO reaction of toluene was inhibited without water vapor. With the instant increase of water vapor and UV off, the concentration peaks (Fig. 3(1)) of molecular mass of 42, 46, 60, 78 and 106 were detected by PTR-MS. In addition, PTR-MS also detected some other gas-phase by-products with very low concentrations (less than 15 ppb) during the water vapor pulse (Fig. 3(2)). They were molecular mass 54, 56, 72, 86 and 122. It indicated that these by-products were generated under lack of water vapor. They were strongly adsorbed on TiO<sub>2</sub> surface and made the deactivation of photocatalyst (Fig. 3). The by-products with molecular mass 32, 42, 44, 58 and 60 were generated if keeping UV on with abundant water vapor (RH: 84%). It shows that the adsorbed by-products on TiO<sub>2</sub> surface should be continuously decomposed into the compounds with small molecular mass. The by-products with molecular mass 42 and 60 were both generated under high and low concentrations of water vapor.

### 3.2. By-products detected via GC–MS

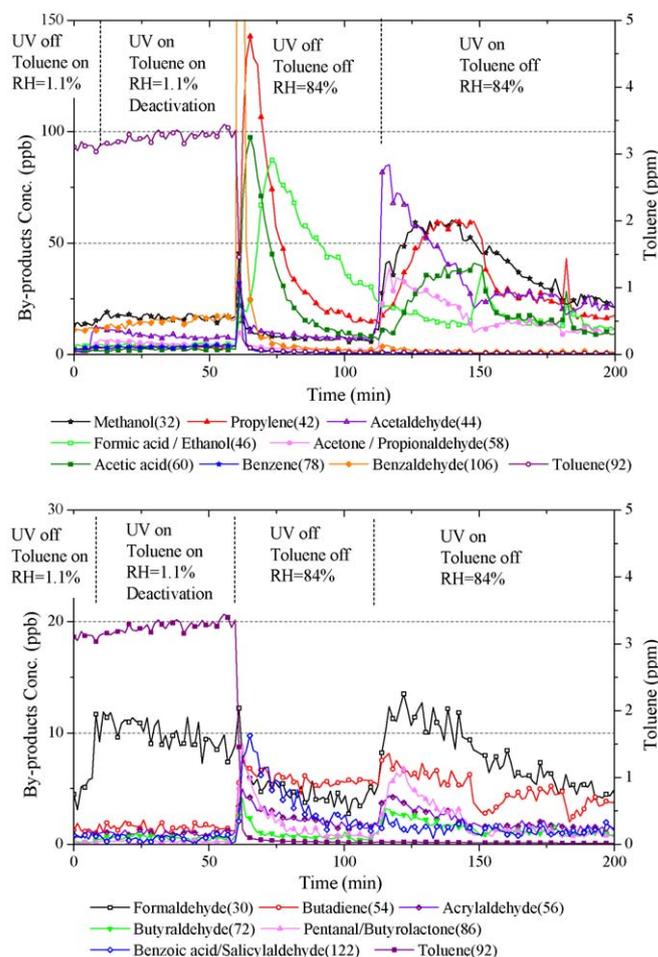
The GC analysis of the extracts after 1 and 2 h of reaction over TiO<sub>2</sub> showed no gas-phase by-products, which agreed with the earlier studies [14,17]. It was due to the low concentration of by-products and the high detection limit of GC. We kept the extract time to be over 10 h and identified part of the by-products by using GC–MS. Table 2 shows the summary of these identified by-products by PTR-MS/GC–MS and their health-related information. The compounds with molecular mass 58, 60, 72, 78, 86, 106 and 122 were respectively identified to be acetone, acetic acid, butyraldehyde, benzene, pentanal, benzaldehyde and benzoic acid. Some by-products found in this study agreed with the literature. d'Hennezel et al. [14] and Irokawa et al. [17] reported that benzaldehyde was the main by-products on the reaction surface. Benzene (molecular mass 78) was identified on the solid surface by Blanco et al. [5] and Martra et al. [20] at very high inlet toluene concentrations after PCO process. In addition, acetic acid (molecular mass 60) and formic acid (molecular mass 46) were also found from PCO decomposition of toluene by d'Hennezel et al. [14].



**Fig. 2.** Toluene and its by-products conversions vs. time with inlet toluene concentration of (1) 8 ppb, (2) 1200 ppb and (3) 450 ppb;  $T = 24\text{--}26\text{ }^{\circ}\text{C}$ ;  $\text{RH} = 47\text{--}50\%$ ;  $254\text{ nm}$ ; UV intensity: (a)  $0.95\text{ mW/cm}^2$ , (b)  $0.78\text{ mW/cm}^2$  and (c)  $0.43\text{ mW/cm}^2$ . (The numbers in brackets are their molecular mass values.)

### 3.3. Photochemical self-decomposition of toluene

The photochemical self-decomposition of toluene was carried out on the blank glass plates with the UV intensities of  $0.95$  and  $0.43\text{ mW/cm}^2$ . The results were shown in the Supplementary



**Fig. 3.** Toluene and its by-products conversions vs. time under water vapor pulse from 1.1% to 84% with inlet toluene concentration of 3200 ppb;  $T = 24\text{--}26\text{ }^{\circ}\text{C}$ ; UV intensity =  $0.43\text{ mW/cm}^2$ . (1) By-products with high concentrations and (2) by-products with low concentrations. (The numbers in brackets are their molecular mass values.)

**Material.** A slight photochemical process only occurred at  $0.95\text{ mW/cm}^2$ . Some by-products, such as formaldehyde, acetaldehyde, acetone, propionaldehyde were found to be generated when the UV-C light irradiated on the blank glass plates. However, the concentrations of these generated by-products were all less than 5 ppb. In addition, the concentration of toluene was not obviously changed after UV on. Thus, the photochemical self-decomposition of toluene had very little influence to the photocatalytic oxidation of toluene due to its low photochemical rate.

## 4. Discussion

### 4.1. Determination of by-products

GC-MS did not detect the compounds with molecular mass 30, 32, 42, 44, 46, 54 and 56 in this study. However, they were identified by PTR-MS (Table 2). Only the compounds with higher proton affinity than water can be detected by PTR-MS [24]. Thus, molecular mass 30, 32, 42, 44, 54 and 56 should respectively be formaldehyde, methanol, propylene, acetaldehyde, butadiene and acrylaldehyde. For the molecular mass 46, it may be formic acid or ethanol. They have the same molecular mass, which cannot be identified through PTR-MS. From Fig. 3, molecular mass 46 (formic acid/ethanol) did not release from the deactivated  $\text{TiO}_2$  surface before the water vapor pulse. It indicated that the compound with molecular mass 46 was strongly adsorbed on  $\text{TiO}_2$  surface. Thus,

**Table 2**  
By-products identified by PTR-MS/GC-MS and their health-related information.

Identified by-products		Probable by-products	NIOSH REL (ppm)	IARC carcinogenic classification
PTR-MS (molecular weight)	GC-MS			
<b>Gas-phase</b>				
30	–	Formaldehyde	0.016	Group 2A, probably carcinogenic to humans
32	–	Methanol	200	–
42	–	Propylene	None established	–
44	–	Acetaldehyde	None established	Group 2B, possibly carcinogenic to humans
46	–	Formic acid	5	–
		Ethanol	1000	–
58	Acetone	Acetone	250	–
		Propionaldehyde	None established	–
60	Acetic acid	Acetic acid	10	–
78	Benzene	Benzene	0.1	Group 1, carcinogenic to humans
106	Benzaldehyde	Benzaldehyde	None established	–
–	Benzyl alcohol	Benzyl alcohol	–	–
–	Phenol, –methyl–	Phenol, –methyl–	–	–
<b>On surface</b>				
54	–	Butadiene	–	–
56	–	Acrylaldehyde	0.1	Group 3, not classifiable as to its carcinogenicity to humans
72	Butyraldehyde	Butyraldehyde	None established	–
86	Pentanal	Pentanal	50	–
	Butyrolactone	Butyrolactone	–	–
122	Benzoic acid	Benzoic acid	None established	–
	Salicylaldehyde	Salicylaldehyde	–	–
<b>Reactant</b>				
92	Toluene	–	100	–

NIOSH: National Institute for Occupational Safety and Health (U.S.); REL: recommended exposure limit; IARC: International Agency for Research on Cancer.

molecular mass 46 was probable to be formic acid, which has stronger adsorption ability than ethanol. In addition, propionaldehyde has the same molecular mass, 58, with acetone. The identified compound, molecular mass 58 is possible to be a mixture of acetone and propionaldehyde.

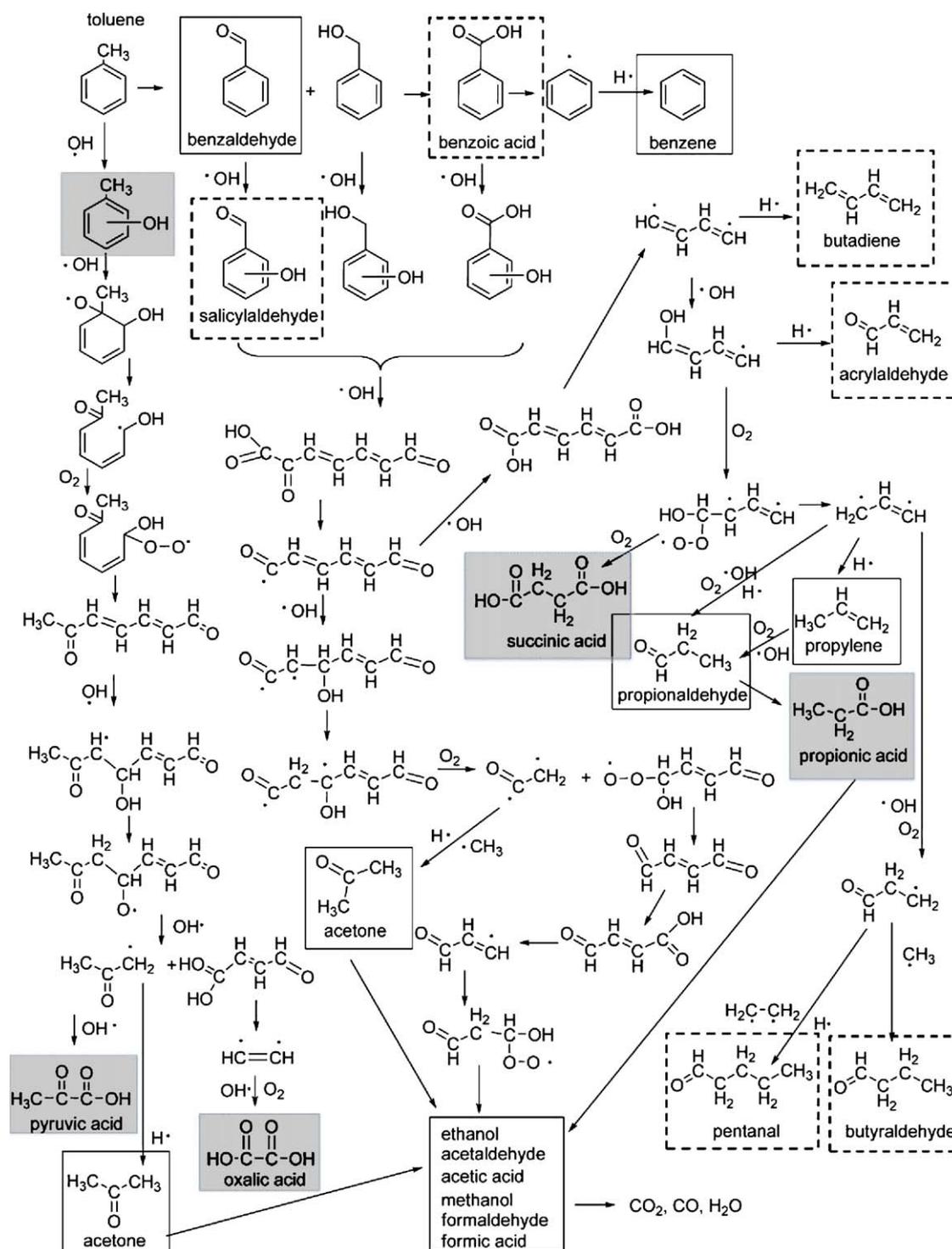
Toluene was first decomposed into benzaldehyde and was then continuously decomposed into some smaller species [6]. At the beginning of UV irradiation, there were a lot of adsorbed toluene and hydroxyl radical (OH<sup>\*</sup>) generated from adsorbed water vapor on TiO<sub>2</sub> surface. Due to the amount of hydroxyl radical being larger than that of toluene, PCO reaction trended to be fully developed. The generated benzaldehyde was fast changed into the compounds with small molecular mass, such as acetaldehyde and acetone/propionaldehyde. It resulted in the peak concentrations of acetaldehyde and acetone/propionaldehyde in Fig. 2. It indicated that acetaldehyde and acetone/propionaldehyde were weakly adsorbed on TiO<sub>2</sub> surface. However, the generated by-products from benzaldehyde to acetaldehyde or acetone/propionaldehyde were strongly adsorbed on TiO<sub>2</sub> surface and blocked its active sites, which made the deactivation of TiO<sub>2</sub>. These by-products had been identified to be benzoic acid, salicylaldehyde, pentanal, butyraldehyde, acrylaldehyde and acetic acid (Table 2).

With PCO reaction continuously running, more and more active sites of TiO<sub>2</sub> were blocked. The decomposition of toluene trended to be incomplete reaction. More and more by-products with big molecular mass were generated, such as benzaldehyde (Fig. 2(1) and (2)). Simultaneously, the concentrations of acetaldehyde and acetone/propionaldehyde decreased. However, this phenomenon did not always happen. When the inlet concentration of toluene was low, few by-products were generated and no deactivation of TiO<sub>2</sub> was found (Fig. 2(3)), that is, toluene trended to be fully decomposed. This observation may result from the abundant UV photons relative to the low toluene concentration.

#### 4.2. Possible PCO pathways of toluene

Most of the previous studies believed that the primary pathway in toluene photocatalytic oxidation is the hydrogen abstraction from the methyl group leading to a benzyl radical and then forming benzaldehyde, benzoic acid and benzyl alcohol [14,18,25]. d'Hennezel et al. [14] gave a detailed photocatalytic oxidation pathways from toluene to benzoic acid. However, the further pathways of the aromatic ring were still not clear enough.

Frankcombe and Smith [26] presented that the first step of toluene oxidation was the addition of an OH radical to the toluene ring followed by donation of the hydrogen atom of the added OH fragment to an O<sub>2</sub> molecule, which led to the corresponding hydroxylated isomers (phenol, –methyl–). Finally, the aromatic ring was opened and formed two carbonyl groups (O=C–R–C=O) at the attacked position, respectively. Based on this mechanism proposed by Frankcombe and Smith [26], it is believable that toluene and its three initial by-products (benzaldehyde, benzoic acid and benzyl alcohol) were attacked by a OH radical addition to the aromatic ring, which resulted in the open of aromatic ring. The compounds generated after ring opening contained several carbonyl bonds (C=O) and alkenyl bonds (C=C). In this study, the main by-products identified in gas phase were all with small molecular mass, which indicated the carbonyl and alkenyl bonds were synchronously or continuously attacked by OH radical and adsorbed oxygen O<sub>2</sub>. It implies that the toluene might react through the pathways: toluene → benzaldehyde → benzoic acids → ring broken → O=C–R–C=C–R'–C=O → shorter-carbon-chain aldehydes and alcohols. This results in the main photocatalytic oxidation pathways of toluene (Fig. 4). The compounds enclosed by full frame were identified in this study. In addition, the by-



**Fig. 4.** Possible photocatalytic oxidation pathways of toluene. Compounds enclosed by solid line, dash line and shadow frame are identified in gas phase, on  $\text{TiO}_2$  surface and reported by earlier lectures, respectively.

products: oxalic acid, pyruvic acid, propionic acid, isovaleric acid and succinic acid shown in Fig. 4 were also detected by Irokawa et al. [17].

The concentration of water vapor strongly influenced the generation of by-products. From Fig. 3, the decomposition of toluene was fast under the condition with abundant water vapor. More by-products with small molecular mass (such as acetaldehyde, methanol) were generated. It resulted from the abundance of hydroxyl radical ( $\text{OH}^*$ ), which derived from the oxidation of adsorbed water vapor.

#### 4.3. Risk assessment of by-products

From Sections 3 and 4, the PCO decomposition of toluene will generate some carcinogenic by-products. It is necessary to evaluate their negative health effect. The risk assessment to human health of these by-products was discussed through a HRI. It is defined as

$$\text{HRI}_i = \frac{C_i}{\text{REL}_i} \quad (1)$$

**Table 3**

The changes of HRI values and sum of carcinogens during PCO decomposition of toluene.

Inlet toluene concentration (ppb)	UV intensity (mW/cm <sup>2</sup> )	HRI <sub>inlet</sub>	Sum of all carcinogens inlet (ppb)	HRI <sub>outlet</sub>	Sum of all carcinogens outlet (ppb)
8000	0.95	0.3	10.1	1.7	79.7
	0.78	0.3	6.8	1.4	63.4
	0.43	0.3	5.1	1.2	56.3
1200	0.95	0.1	4.3	0.7	28.6
	0.78	0.1	3.7	0.7	29.7
	0.43	0.1	4.6	0.8	29.5
450	0.95	0.1	4.8	0.6	26.2
	0.78	0.1	5.3	0.5	16.6
	0.43	0.1	4.9	0.3	10.8

where  $REL_i$  is the recommended exposure limit of compound  $i$ . Some institutes have published the REL values of various VOCs (Table 2), such as U.S. NIOSH (National Institute for Occupational Safety and Health) [27]. It is required that HRI, the sum of all HRI<sub>*i*</sub>, should not exceed the value 1.

$$HRI = \sum_i HRI_i \leq 1 \quad (2)$$

Table 3 shows the HRI changes during PCO decomposition of toluene (except the compounds without REL value). HRI values of outlet were always larger than that of inlet. The sum of all carcinogens increased after PCO reaction. It means that some more harmful by-products were generated during PCO process, such as formaldehyde, benzene and acetaldehyde (Table 2). Especially, HRI values of outlet exceeded 1 when the inlet toluene was 8 ppm. It means the inlet air after being treated by PCO will become more harmful. However, it is not right to adjudge PCO as a useless technology for indoor air cleaning. Because of the specific pollutant in this study, toluene is not a very harmful product to human (the REL value of toluene is 100 ppm by NIOSH). Furthermore, most of the HRI values were actually smaller than 1 under low inlet toluene levels (Table 2). Although, some undesired by-products were generated, it seems that these by-products may not have negative effects to human health because of their low concentrations. It is expected that PCO may decrease the HRI values for some carcinogenic pollutant, such as benzene.

## 5. Conclusions

In this study, the by-products at ppb level were studied during PCO decomposition of toluene in a plate-type reactor and identified using PTR-MS and GC-MS. The process of their generations was traced and analyzed by adjusting initial toluene and water concentrations. It was found that benzaldehyde, methanol, acetaldehyde, acetone/propionaldehyde, formic acid/ethanol and acetic acid were the main by-products in the gas phase. By adjusting the concentration of water vapor, some compounds adsorbed on the TiO<sub>2</sub> surface were ascertained, which resulted in the deactivation of TiO<sub>2</sub>. They were benzoic acid, benzene, acrylaldehyde, butyraldehyde and pentanal. Besides, we have shown that the absence of water vapor not only decreased the degradation rate of toluene, but also infect the generation of its by-products (types and concentrations). Moreover, the by-products of formaldehyde, methanol, propylene, acetaldehyde and acetone/propionaldehyde have not been reported in the literature. Our experimental results support possible photocatalytic oxidation pathways of toluene. A HRI was introduced to assess the risk level to human health of these ppb-level by-products. It concludes that although some undesired by-products (even carcinogenic) are generated during PCO decomposition of toluene, it seems that

these by-products do not have negative effects to human health because of their low concentrations. This work is of great importance for the application of PCO technology indoor environment field.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2009.01.015.

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