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Photodegradation of xylene isomers: Kinetics, mechanism, secondary pollutant formation potential and health risk evaluation

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ABSTRACT

Photodegradation technology has been widely applied in the purification of industrial aromatic hydrocarbons. However, whether this technology efficiently removes the pollutants to prevent secondary pollution and health risk is still unclear. Here, the photodegradation processes of three xylenes were compared under designed reaction atmospheres and light sources. Xe lamp showed poor photodegradation ability toward xylenes, no matter in N_2 or N_2+O_2 system, while much higher photodegradation performance of xylenes were obtained under ultraviolet (UV) and vacuum ultraviolet (VUV) irradiation, especially in N2+O2+VUV system, where 97.9% of m-xylene, 99.0% of o-xylene or 87.5% of p-xylene with the initial concentration of 860 mg/m³ was removed within 240 min. The xylenes underwent three processes of photo-isomerization, photodecomposition and photo-oxidation to produce intermediates of aromatics, alkanes and carbonyls. Among them, the photo-isomerization products showed the highest concentration percentage (e.g., 250% in o-xylene system), confirming that photo-isomerization reaction was the dominated photodegradation process of xylenes. Moreover, these isomerized products not only contributed about 97% and 91% to the formation potential of O_3 (OFP) and secondary organic aerosols (SOAFP), but also displayed obvious non-carcinogenic risk, although one of photodecomposition productbenzene showed the highest occupational exposure risk. Therefore, the secondary pollution and health risks of photodegradation products of xylenes were non-ignorable, although the OFP, SOAFP and health risks of the generated products reduced at least 4.5 times in comparison with that of the degraded xylenes. The findings are helpful for the appropriate application of this technology in the purification of industrial organic waste gas.

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Introduction

With the accelerated development of industrialization and urbanization, the emission from industrial organic waste gases has become an increasingly important source of air pollu-

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tion in China (Yan et al., 2018). Aromatic hydrocarbons (AHs) are one main group of the pollutants in industrial organic waste gases (He et al., 2012; Ho and Lee, 2002; Lin et al., 2023; Zhang et al., 2018). AHs have also been considered as a main source of secondary pollutants such as O_3 and secondary organic aerosols (SOA) in the atmospheric environment (Zhang et al., 2018; Korologos et al., 2012), threating local air quality and human health (Healy et al., 2009). Therefore, developing effective technology to eliminate the emission of AHs from industrial processes is urgent.

At present, there are many effective technologies to remove industrial AHs, including non-destructive technologies such as adsorption and absorption, and destructive technologies such as biodegradation, thermal catalysis and Photocatalysis (Chen et al., 2022; Dal Pozzo et al., 2017; Ma et al., 2011). Among the technologies that have been applied in the field, the photocatalysis technology using sunlight as light source has been paid more attention (Chen et al., 2016a, 2016b; Chen et al., 2021b; Liu et al., 2017). AHs can be removed in the following three ways, i.e., direct decomposition by light, and respective degradation in the gas phase and on the catalyst interface by reactive oxygen species. In theory, industrial emitted AHs can be well eliminated by photocatalysis technology. However, in most field applications of the photocatalysis technology, the catalyst module is always unemployed due to cost consideration, resulting in the existence of only two processes of direct decomposition by light and degradation in the gas phase by reactive oxygen species work. Such so-called "photocatalysis technology" is actually photodegradation technology as known. However, it is not clear whether the removal of industrial AHs by direct photodegradation will cause secondary pollution and thus affect human health.

Over the past few decades, the photodegradation technology has been attempted to apply in the treatment of different organic pollutants in the laboratory under different experimental parameters (Bhowmick and Semmens, 1994; Chen et al., 2007; Hand et al., 1986; Lee et al., 2017; Shen and Ku, 1997, 1998; Shen et al., 1995; Wang and Ray, 2000). For example, Chen et al. studied the photodegradation of chlorinated alkane and alkene, and found different effects of the experimental parameters (initial VOCs concentration, reaction medium, relative humidity, light intensity, temperature and mixture) on the photodegradation kinetics and mechanisms of the substrates (Feiyan et al., 2002). Also, the authors observed formation of higher molecular weight intermediates and polymers in nitrogen reaction medium, which were difficult to be mineralized by further photodegradation. These refractory intermediates may further form secondary pollutants after their discharge, affecting the quality of atmospheric environment. Recently, Zhang et al. studied the formation of SOA during photodegradation of xylene with the present of NOx and proved that the oligomerization of ring opening products of xylene dominated SOA formation (Zhang et al., 2019). The photodegradation products of organics not only affect the environment, but also show health risk to human. Feng et al. observed more recalcitrant and toxic intermediates emerged during the photodegradation of dimethyl phthalate (Feng et al., 2022).

If the photodegradation technology is applied in the industrial AHs elimination, whether or not the secondary pollution and health risk appear during the treatment process is of great concern. Although the impact of atmospheric photochemical process of AHs with ambient concentration to the SOA formation and human health risk has been explored (Dhada et al., 2015; Huang et al., 2007, 2010; Kleindienst et al., 2004; Song et al., 2007), there is still a lack of systematic research on the photodegradation process of AHs from industrial emission, including degradation kinetics, products, mechanisms, and environmental and health effects.

Therefore, in this study, photodegradation of three representative AHs, m-xylene, o-xylene and p-xylene, was investigated. The effects of light sources and reaction atmosphere on the photodegradation kinetics of these AHs were discussed. Moreover, the photodegradation products in different systems were qualitatively and quantitatively analyzed to propose the possible photodegradation pathways and mechanisms of xylenes. Furthermore, the formation potentials of O_3 (OFP) and SOA (SOAFP) as well as the non-carcinogenic and occupational exposure risks during photodegradation of xylenes were evaluated. Finally, the OFP, SOAFP and health risk of the degraded xylenes and their photodegradation possibility of the photodegradation technology.

1. Materials and methods

1.1. Photodegradation experiments

The designed amount of liquid xylene (purity≥99.9%, Beijing Bellwether Co., Ltd., China) was directly injected into a selfmade Pyrex glass reactor (vol. 5 L) (Chen et al., 2019) filled with high-purity N₂ (99.99%) or N₂+O₂ (99.99%, V/V=4:1) to achieve the initial concentration of about 860 mg/m³. The relative humidity in the reactor was about 5%. Three different lamps (Xenon (Xe), PLS-SXE300, Beijing Bofeilai Technology Co., Ltd., China; UV_{254 nm} (UV), Guangdong Xuelaite Optoelectronic Technology Co., Ltd., China and UV_{185+254 nm} (VUV), Guangdong Xuelaite Optoelectronic Technology Co., Ltd., China) were used as light sources, which irradiated the reactor from the top through a quartz window. The absorption wavelengths of three xylenes were less than 330 nm (Appendix A Fig. S1a), which partially overlapped the irradiation wavelength of the three lamps (Appendix A Fig. S1b). These results indicated that the selected lamps could initiate photolysis of xylenes. Then, at the fixed intervals, 1 mL of gas sample in the reactor was sampled by an automatic sample injection system equipped on a gas chromatograph (GC9800, Shanghai Kechuang Chromatographic Instrument Co., Ltd., China) to determine the concentration of xylene. The temperatures of column (DB-5MS), inlet and detector in the GC were set at 120°C, 200°C and 250°C, respectively. High purity N₂ was used as carrier gas with a flow rate of 100 mL/min.

1.2. Qualitative and quantitative analysis of gaseous intermediates

After 120 min reaction, the gaseous sample was also collected using a vacuum Summa canister (vol. 2.7 L, Silonite TM, ENTECH Instruments Inc., USA). During sampling process, a Teflon bag filled with 3 L high purity N₂ and the canister were separately connected to two sides of the reactor. After simultaneously opening the valves of the bag and canister, the gas sample in the reactor was inhaled into the canister and the N₂ in the bag entered into the reactor. The analysis of the collected samples in the canister was carried out by a combining Entech 7200 pre-concentration system (Entech Instruments Inc., CA, USA) with gas chromatography-mass spectrometry (GC-MS, 7890B GC-5977B MS, Agilent Technologies, USA). A DB-5 column (60 m imes 0.32 mm imes 0.25 μ m, Agilent Technologies, USA) was used with the GC oven temperature program: initially 35°C for 5 min, programmed to 150°C at a rate of 5°C/min, and then to 250°C at a rate of 15°C/min which was held for 2 min. The carrier gas was ultrahigh purity helium at a constant flow rate of 1.2 mL/min. Mass spectrometer conditions were as follows: ionizing energy: 70 eV, scan range: 45-260/me, temperature of the transfer line: 290°C. The analysis method was referred to TO-15 of US Environmental Protection Agency (Conley et al., 2005). A detailed description of analysis procedures has been published in previous study (Chen et al., 2021a).

The external standard method was applied for the qualitative and quantitative analysis of the compounds according to the retention time, mass spectrum and peak area of the studied sample and the standard sample. The standard curve for each compound was established by diluting the TO-15 standard sample (1000 ppbv, Linde Spectra Environment Gases, USA) to 20, 30, 60, 200 and 300 ppbv by an Entech 4700 dynamic diluter.

1.3. Quality assurance and quality control

The Summa canister was flushed with high purity N_2 before being used and evacuated to 8 ± 1 Pa. All collected samples were analyzed within 7 days after sampling. All the calibration standard curves were justified with the correlation coefficients (R^2) over 0.995 (**Appendix A Fig. S2**). Before sample analysis, the analytical system was checked with a one-point calibration. If the response was beyond 5% of the initial calibration curve, a re-calibration was performed. More information of quality assurance and quality control has been published in previous study (Chen et al., 2021a).

1.4. Secondary pollutant formation assessment

1.4.1. OFP

OFP referred to the maximum reaction activity of volatile organic compounds (VOCs) to generate O_3 based on release and reaction activity under the premise of optimal reaction conditions and determined key species and sources (Liu et al., 2019; Ou et al., 2015). The maximum incremental activity (MIR) method was often used to characterize the photochemical activity of O_3 produced by various VOCs (as shown in **Appendix A Table S1**). The calculation equation of OFP was as follows:

$$OFP_i = C_i \times MIR_i \tag{1}$$

where, OFP_i is the OFP of VOCs component i, C_i (µg/m³) is the concentration of VOCs component i, and MIR_i is the maximum incremental activity value of VOCs component i (Carter, 2008).

1.4.2. SOAFP

SOAFP of VOCs in the atmosphere was calculated by the following equation (Zhang et al., 2017):

$$P_{SOAP_{i}} = \frac{\sum (VOC_{i} \times SOAP_{i})}{100} \times FAC_{toluene}$$
(2)

where, SOAP_i is the SOAFP parameter of VOCs component i (toluene was assumed to be 100) (Derwent et al., 2010). The detailed parameters were shown in Appendix A Table S1. VOC_i (µg/m³) is the concentration of VOCs component i and $FAC_{toluene}$ (%) is the fractional aerosol coefficient of toluene and chosen as 5.4% according to previous study (Zhang et al., 2017).

1.5. Health risk assessment

1.5.1. Non-carcinogenic risk

The non-carcinogenic risk (HR) of VOCs was defined as the ratio of the average daily VOCs concentration inhaled to the corresponding reference concentration (RfC_i), which was calculated as follows (An et al., 2014; Li et al., 2013):

$$HR_i = \frac{C_i}{RfC_i}$$
(3)

where, C_i (µg/m³) is the concentration of the target compound i, and RfC_i (µg/m³) is the non-carcinogenic reference concentration of the target compound i (**Appendix A Table S2**). HR great than 1.0, between 0.1 and 1.0, and less than 0.1 indicated that VOC had a definite, possible and negligible non-carcinogenic, respectively.

1.5.2. Occupational exposure cancer risk

The occupational exposure cancer risk (E_i) of workers through respiratory exposure to VOCs was assessed by referring to the health assessment method in the previous studies (An et al., 2014; Liu et al., 2017). Occupational exposure risk was the ratio of the concentration (C_i) of target VOC to its limit-timeweighted mean (TLV-TWA_i). The total occupational exposure risk was the sum of occupational exposure risk of each target compound, and the calculation was shown in the Eqs. (4) and (5).

$$E_i = \sum_{i=0}^n \frac{C_i}{TLV - TWA_i} \tag{4}$$

$$\sum E = \sum E_i \tag{5}$$

where, TLV-TWA_i is that workers worked 8 hr a day and 5 day a week, and its value is shown in **Appendix A Table S2**. If E_i was greater than 1.0, it indicated that exposure to VOC component at this concentration was harmful to worker's health. If E_i was less than 1.0, it indicated that there was no harm to worker's health.

2. Results and discussion

2.1. Photodegradation kinetics of xylenes

Fig. 1 shows the photodegradation kinetics curves of three xylenes under different reaction atmospheres and light



Fig. 1 – Photochemical kinetic curves of xylenes under different conditions.

sources. Under N₂ atmosphere, about 5.5% of m-xylene, 19.0% of o-xylene and 3.3% of p-xylene were photodegraded after 240 min reaction. All these efficiencies increased to 6.9%, 20.0% and 19.3% when the atmosphere was replaced by N₂+O₂. The presence of O₂ slightly enhanced the photodegradation of all xylenes. However, Xe lamp irradiation could not achieve highly efficient decomposition of the xylenes under the both N₂ and N₂+O₂ atmospheres. This was due to that xylenes (main absorption wavelength \leq 330 nm) was difficultly photodecomposed by the light of Xe lamp (dominated wavelength > 400 nm). Further comparison revealed that o-xylene showed the highest photodegradation efficiency among the xylenes under both N₂ and N₂+O₂ atmospheres irradiated by Xe lamp.

When Xe lamp was replaced by UV lamp, increasing photodegradation efficiency of xylenes was obtained. About 58.2% and 47.8% of m-xylene, 67.1% and 59.4% of o-xylene, and 48.3% and 58.7% of p-xylene were degraded under N₂ and N₂+O₂ atmospheres, respectively. The significantly enhanced

photodegradation efficiencies of all xylenes by UV irradiation was due to the higher photon energy of UV than Xe lamp (Chen et al., 2019). Comparing with N2+UV system, relatively lower photodegradation efficiencies of m-xylene (42.8%), o-xylene (50.3%) and p-xylene (43.5%) were obtained in N2+VUV system, due to weaker intensity of VUV than UV (see Appendix A Fig. S1b). Interestingly, about 97.9% of m-xylene, 99.0% of o-xylene and 87.5% of p-xylene were removed within 240 min in N₂+O₂+VUV system. Furthermore, in N_2+O_2+VUV system, the rate constants (calculated via equation of $-\ln(C/C_0) = kt$, where C_0 was the initial concentration of xylene and k was the rate constant) of three xylenes ranged from 3.65 imes 10⁻³/min to 4.13 imes 10⁻³/min, which were at least 1.5 times of that in other systems (Appendix A Fig. S3). The formation of reactive oxygen species (e.g., O_3 , $O(^1D)$, $O(^3P)$) from the reaction of VUV photons and O2 molecule in this system was responsible for the remarkably enhanced degradation efficiency of all xylenes. Weon et al. reported that the VUV photolyzed O₂ into O(1 D) and O(3 P) and then O(3 P) reacted



Fig. 2 – Total ion chromatograms ((a)-(f)) and concentrations ((g)-(l)) of intermediates from xylenes under different experimental conditions.

with O_2 to generate O_3 , while these generated ROS further oxidized the organics (Weon et al., 2019), supporting the present results.

To sum up, Xe lamp showed poor photodegradation ability toward all xylenes, no matter in N_2 or N_2+O_2 system. In comparison, UV and VUV displayed much higher photodegradation performance to xylenes in both N_2 and N_2+O_2 system. Notably, almost complete degradation of all xylenes was achieved in N₂+O₂+VUV system. In N₂ system, the degradation of xylene was completely relied on the photons from the lamp emission to break the molecular bond. Different emission wavelength of the Xe, UV and VUV resulted in the different energy of the emitted photons. In theory, the shorter wavelength of the light was, the stronger photo energy was. For example, the light photons at 185 and 254 nm had the energies of 647 and 471 kJ/mol, respectively (Kiattisaksiri et al., 2016). Meanwhile, the photo energy from UV was enough to break the π bond (264 kJ/mol) of C=C bond in xylenes (Chen et al., 2019). Thus, the UV and VUV showed almost equal photodegradation performance toward xylenes, but higher than Xe lamp. When the present of O₂, VUV rather than Xe and UV could break the O=O covalent bond (494 kJ/mol) of O₂ (Huheey et al., 1993), producing various ROS to further degrade xylenes and achieve their high photodegradation efficiency.

2.2. Composition and concentration of photodegradation intermediates of xylenes

In order to investigate the effects of reaction atmosphere and light source to the composition and concentration of these intermediates, the gaseous samples after reaction for 120 min under different experimental conditions were sampled and analyzed. As shown in Fig. 2a, photodegradation of mxylene, o-xylene and p-xylene in N₂+Xe system resulted in nine peaks, corresponding to the compounds of n-hexane (A₁), benzene (A₂), toluene (A₃), ethylbenzene (A₄), p-xylene (A₅), m-xylene (A₆), o-xylene (A₇), isopropyl benzene (A₈) and 1,3,5trimethylbenzene (A₉) (**Appendix A Table S3**). Photodegradation of m-xylene, o-xylene and p-xylene produced their isomers, suggesting occurrence of photo-induced isomerization reaction of xylenes. Moreover, n-hexane was detected in all systems, indicating that ring-opening reaction happened on all xylenes after Xe irradiation. When O₂ was added into N_2 +Xe system, a new oxygenated product, acetone (A_0), was identified accompanying with above nine hydrocarbon products after photodegrading xylenes for 120 min (Fig. 2b and Appendix A Table S4). This result confirmed that the presence of O₂ further oxidized the hydrocarbon products. Furthermore, the photodegradation of xylenes in N_2+UV (Fig. 2c and Appendix A Table S5) and N₂+VUV (Fig. 2e and Appendix A Table S7) systems led to similar compositions of products as that in N₂+Xe system, while product compositions in N₂+O₂+UV (Fig. 2d and Appendix A Table S6) and N₂+O₂+VUV (Fig. 2f and Appendix A Table S8) systems were similar as that in N₂+O₂+Xe system. Clearly, photodegradation of xylenes by different light sources resulted in similar product composition under the same reaction atmosphere, although the xylenes displayed very different photodegradation efficiency under Xe, UV and VUV irradiation.

Further quantification analysis of these intermediates was conducted to investigate the concentration variation of them under different experimental conditions. As shown in Fig. 2g, photodegradation of m-xylene in N_2 +Xe system for 120 min produced 27.0 ppbv of n-hexane (A_1) , 0.6 ppbv of benzene (A_2) , 14.0 ppbv of toluene (A₃), 11.5 ppbv of ethylbenzene (A₄), 0.7 ppbv of p-xylene (A₅), 322.0 ppbv of o-xylene (A₇), 23.3 ppbv of isopropyl benzene (A₈) and 4.0 ppbv of 1,3,5-trimethylbenzene (A_9) . Clearly, the highest concentration of the product was o-xylene, one of m-xylene's isomer, accounting for 79.9% of the total concentration of all products. As for o-xylene and p-xylene, their photodegradation products with the highest concentration and percentage were m-xylene (1942.5 ppbv and 81.9%) and o-xylene (587.5 ppbv and 53.2%), respectively. These results suggested that the photo-isomerization reaction was the dominant photodegradation route for xylenes in N₂+Xe system. Moreover, the total concentration of all products from o-xylene (2373.7 ppbv) was higher than m-xylene (403.6 ppbv) and p-xylene (1105.3 ppbv), due to its highest photodegradation efficiency.

As for N₂+O₂+Xe system, photodegradation of m-xylene produced 197.5 ppbv of acetone (A₀), 5.3 ppbv of n-hexane (A₁), 0.3 ppbv of benzene (A₂), 8.5 ppbv of toluene (A₃), 3.0 ppbv of ethylbenzene (A₄), 0.4 ppbv of p-xylene (A₅), 229.0 ppbv of o-xylene (A₇), 6.5 ppbv of isopropyl benzene (A₈) and 1.0 ppbv of 1,3,5-trimethylbenzene (A₉) (Fig. 2h). The concentrations of products A₁ to A₉ all decreased in N₂+O₂+Xe system comparing with that in N₂+Xe system, while the newly formed product of acetone (A_0) showed the second highest concentration among all products. These results suggested that O_2 further oxidized the products A_1 - A_9 of xylenes to A_0 . Further calculation revealed that the percentages of o-xylene and acetone were 50.7% and 43.7%, implying that both photoisomerization and photo-oxidation reactions were main photodegradation processes for m-xylene in N_2+O_2+Xe system. Similarly, m-xylene (498.5 ppbv and 50.7%) and acetone (219.2 ppbv and 22.3%) or o-xylene (216.5 ppbv and 38.3%) and acetone (103.6 ppbv and 18.3%) ranked the top two concentration and percentage of products from o-xylene or p-xylene photodegradation, further confirming above speculation. Also, the total concentration of all products from o-xylene (982.7 ppbv) was higher than m-xylene (451.5 ppbv) and p-xylene (565.9 ppbv), consistent with the trend of photodegradation kinetics results.

In comparison with N₂+Xe or N₂+O₂+Xe system, photodegradation of xylenes produced higher concentration of intermediates in N₂+UV (ranging from 1659.7 to 6471.2 ppbv) and N₂+VUV (ranging from 2330.3 to 11561.3 ppbv) systems or in N₂+O₂+UV (ranging from 838.6 to 1463.5 ppbv) and N₂+O₂+VUV (ranging from 1006.7 to 3071.4 ppbv) systems (Fig. 2i-2l). Clearly, the VUV system produced higher concentration intermediates than UV and Xe systems, due to its highest photodegradation ability toward xylenes. Similar to Xe system, the presence of O₂ could improve the photodegradation of xylenes and produce higher concentration intermediates in UV and VUV systems.

Further analysis revealed that o-xylene (999.0 ppbv) and n-hexane (262.0 ppbv), or m-xylene (4785.0 ppbv) and n-hexane (1104.5 ppbv) were top two highest concentrated intermediates from photodegradation of m-xylene or o-xylene in N_2 +UV system. As for p-xylene, its photodegradation products of o-xylene (426.0 ppbv) and n-hexane (666.5 ppbv) also showed relatively high concentrations. All these results indicated that xylenes tended to occur the photo-isomerization and ring-opening reactions in the N_2 +UV system. Furthermore, the concentrations of n-hexane in N_2 +O₂+UV and N_2 +O₂+VUV systems were in the range of 22.3 to 78 ppbv and 7.9 to 168.0 ppbv, respectively. Clearly, the presence of O₂ efficiently suppressed the ring-opening of xylenes to form n-hexane.

In addition, the concentrations of o-xylene, m-xylene and o-xylene from photodegradation of m-xylene, o-xylene and p-xylene were 323.5 (or 690.0), 928.5 (or 2226.0) and 244.0 ppbv in N₂+O₂+UV (or N₂+O₂+VUV) system, showing the highest concentration among all products in the same reaction system. The concentration of o-xylene from photodegradation of p-xylene was 367.0 ppbv in N₂+O₂+VUV system, ranking the second place of concentration among all products. The photoisomerization reaction was also very important for xylenes in all studied systems.

It should be noted that much higher concentration of isopropyl benzene was obtained from photodegradation of oxylene (298.0 ppbv in average) than m-xylene (49.1 ppbv in average) and p-xylene (9.5 ppbv in average) in the studied systems, suggesting more easily transformation of o-xylene to isopropyl benzene. Moreover, benzene, toluene and ethylbenzene produced from photodegradation of p-xylene (129.8, 314.2 and 126.6 ppbv) showed higher average concentration than m-xylene (20.5, 120.9 and 18.7 ppbv) and o-xylene (32.1, 115.1 and 10.5 ppbv), indicating favorable conversion of p-xylene to benzene, toluene and ethylbenzene.

Dhada et al. reported that n-hexane was the dominant gaseous intermediate from photocatalytic degradation of oxylene (Dhada et al., 2016), consistent with the present results that xylenes underwent ring-opening reaction to form n-hexane. Mo et al. found the photocatalytic degradation of toluene to acetone (Mo et al., 2009), strongly agreeing with the present conclusion of O₂ accelerating the transformation of xylene's intermediates to acetone. Chen et al. studied the photocatalytic degradation of styrene, while benzene, toluene, ethylbenzene and acetone were identified as gaseous intermediates (Chen et al., 2019), supporting the results in this study. Moreover, these authors proposed that the cycloisomerisation of styrene to benzocyclobutene was the initial step of photocatalytic degradation processes, solidly proving the present conclusion that photo-isomerization reaction of xylenes dominated in all studied systems.

2.3. Photodegradation pathway and mechanism of xylenes

Based on the intermediate information, the possible photodegradation pathways and mechanisms of xylenes were proposed. As shown in Fig. 3, the overall reaction pathways were divided into three parts: photo-isomerization, photodecomposition and photo-oxidation. Specifically, the xylene molecule first absorbed the photogenerated photons from light irradiation. If the photon energy was enough to excite the xylene molecule from the ground state to the excited state, the self-isomerization reaction of xylenes was triggered. Then, the interconversion among m-xylene, o-xylene and p-xylene was observed in this study. The isomer products showing the highest concentration among all products revealed that the photo-isomerization reaction was the most important photodegradation pathways for xylenes. It was known that the xylene isomerization reactions were often used to select and separate xylenes during industrial processes (Bauer et al., 2004; Tarach et al., 2017). The processes often consisted of three main transformation reactions, including protonation, dealkylation and alkyl transfer (John et al., 1999). In addition, there were fewer para isomers in equilibrium (Cappellazzo et al., 1991; Gonçalves and Rodrigues, 2013), consistent with the results in this study that p-xylene in the isomerization products was significantly lower than that of oxylene and m-xylene.

When the energy of partial photons exceeded the energy of C-C bond connecting the side-chain methyl group and phenyl ring in xylenes, the gradually loss of side-chain methyl group happened to successively form toluene and benzene. At the same time, these photons broke the π bond of phenyl ring to generate alkane, such as n-hexane. During these processes, the produced n-hexane, toluene and benzene displayed relatively higher concentration, suggesting that photodecomposition reaction pathways also contributed significantly to xylene photodegradation. Sandro et al. reported that toluene was generated by the replacement of hydrogen and methyl



Fig. 3 - Schematic diagram of photodegradation pathway and mechanism of xylenes.





(Gail and Dagaut, 2007), partially supporting the present results.

It should be noted that in N₂ system, the photodegradation of xylenes only underwent the photo-isomerization and photodecomposition pathways. When O₂ was involved into the N₂ system, photo-oxidation reactions of xylenes and their intermediates were also triggered. In the N₂+O₂ system, the xylenes and their products could be directly oxidized by O₂ to form acetone, and finally CO₂ and H₂O. Notably, under the effect to VUV, O₂ was also converted to reactive oxygen species (e.g., O₃, O(¹D), O(³P)). These species efficiently oxidized the xylenes and their products to acetone, CO₂ and H₂O. The much higher photodegradation efficiency of xylenes in N₂+O₂+VUV system than in N₂+VUV system confirmed the significant role of photo-oxidation pathways of xylenes.

2.4. OFP and SOAFP from photodegradation intermediates of xylenes

VOCs are an important group of organics in atmospheric troposphere. The photodegradation of VOCs in atmospheric environment produces secondary pollutants such as O₃ and SOA, which not only affect atmospheric visibility and global climate change, but also pose a serious threat to human health. Therefore, the OFP, SOAFP and health risk (see Section 2.5) of xylenes in different photodegradation systems were investigated. Fig. 4a-4f show the OFP of three groups of products (aromatics, alkanes and carbonyls) from photodegradation of xylenes in different systems. As shown in Fig. 4a, photodegradation of m-xylene, o-xylene and p-xylene for 120 min resulted in OFP concentrations of 1.26×10^{-2} , 9.56×10^{-2} and 2.70×10^{-2} µg/m³ in N₂+Xe system. This result indicated that the photodegradation products from o-xylene more significantly contributed to the O_3 formation than its isomers. Further comparison revealed that higher than 99.2% of OFP was contributed from aromatics intermediates of xylenes.

Similarly, much higher OFP concentration was obtained from photodegradation of o-xylene ($2.68 \times 10^{-2} \mu g/m^3$) than m-xylene ($0.88 \times 10^{-2} \mu g/m^3$) and p-xylene ($1.06 \times 10^{-2} \mu g/m^3$) in N₂+O₂+Xe system (Fig. 4b). However, the OFP concentrations of xylenes in N₂+O₂+Xe system were all smaller than that in N₂+Xe system. This trend was also observed in UV and VUV systems (Fig. 4c-4f). The reason was due to production of higher concentrated intermediates in the pure N₂ system. Further comparison indicated that the OFP concentration in the N₂ and N₂+O₂ systems irradiating by different lamps obeyed the order of Xe < UV < VUV. Such order was consistent with the order of the intermediate concentration, solidly proving the potential contribution of these products to O₃ formation during photodegradation of xylenes.

In addition, among three groups of products (aromatics, alkanes and carbonyls), it was found that the contribution of aromatic products (>99%) to OFP concentration was dominant in Xe, UV and VUV systems. Therefore, the contribution of each aromatic product to OFP concentration was further investigated. As shown in Fig. 4g-4h, during photodegradation of m-xylene, o-xylene or p-xylene in N₂+Xe and N₂+O₂+Xe systems, the highest OFP concentrations were obtained from o-xylene (0.82 \times 10^{-2} and 1.16 \times 10^{-2} $\mu\text{g/m}^3\text{)}\text{,}$ m-xylene (2.30 \times 10^{-2} and 8.96 \times 10^{-2} $\mu\text{g/m}^3)$ or o-xylene (0.78 \times 10^{-2} and 2.11 \times 10^{-2} $\mu g/m^3$), accounting for 96.0% and 92.3%, 86.6% and 93.8% or 74.0% and 78.7% of the total aromatic products. Similar phenomenon was also observed in UV and VUV systems (Fig. 4i-4l). All these consistent results confirmed that the photo-isomerization products of xylenes dominantly contributed to the OFP concentration in this study.





In other words, the photo-isomerization pathways of xylenes were more significantly in O₃ formation than photodecomposition and photo-oxidation pathways. However, toluene accounted for 26.1% and 35.6% of contributions to OFP concentrations in N₂+O₂+UV and N₂+O₂+VUV systems, suggesting that the photodecomposition pathway was also an important contributor to O₃ formation during photodegradation of xylenes.

Similar to OFP results, the SOAFP concentration from oxylene photodegradation was the highest among all xylenes in the studied systems and aromatics products dominated the contribution of SOAFP concentration among all products (Fig. 5a-5f), confirming that the photodegradation products of o-xylene, especially aromatics, significantly contributed to the formation of both O_3 and SOA. Previous studies have also confirmed the important contribution of aromatics to the formation of secondary air pollutants (Ou et al., 2015), partially supporting the present results.

Further analysis of the contribution of individual aromatic product to SOAFP concentration revealed that the isomerization product of m-xylene and o-xylene accounted for higher than 78.3%% and 86.6% among all products (Fig. 5g-5f). These results were consistent with the OFP results, revealing that the photo-isomerization reaction of these two xylenes were more significantly in O3 and SOA formation. As for p-xylene, the oxylene and toluene accounted for 54.2% to 78.7% and 8.5% to 35.6% of SOAFP concentration, respectively. Further comparison revealed the higher contribution percentage of toluene in SOAFP concentration in UV and VUV systems than Xe system. Derwent et al. estimated the SOAFP of 113 VOCs through atmospheric oxidation and found that simple C6-C8 aromatic compounds, such as toluene, ethylbenzene and xylene isomers, had a strong tendency to form SOA (Derwent et al., 2010), supporting the present results. Wu et al. also reported that alkyl benzene was the largest contributor to OFP and SOAFP, and toluene and xylene were the single VOCs species with the largest contributors (Wu et al., 2017), consistent with the current conclusions. All these indicated that both photoisomerization and photodecomposition pathways were important contributor to SOA formation during photodegradation of p-xylene, especially in UV and VUV systems. It was also noticed that the contribution percentage of toluene in SOAFP was much higher than that in OFP from photodegradation of p-xylene, implying that the photodecomposition pathways showed more important role in the formation of SOA than O_3 .

2.5. Non-carcinogenic and occupational exposure cancer risks of products from photodegradation of xylenes

The non-carcinogenic risk of each product obtained in different systems was assessed and the results are shown in the top image of Fig. 6. In N2+Xe system, the HRs of nhexane from m-xylene, o-xylene and p-xylene were 0.2, 0.1 and 0.1, revealing potential non-carcinogenic risk concern associated with this product based on the assessment standard (McCarthy et al., 2009). Interestingly, the HRs of n-hexane from all xylenes decreased to 0.03 in N₂+O₂+Xe system, indicating negligible non-carcinogenic risk concern associated with such product at current system. The further oxidation of nhexane by O₂ to other products, such as acetone, was responsible for the decreased non-carcinogenic risk of n-hexane. As shown in N_2+O_2+Xe system, the HRs of acetone from three xylenes were in the range of 2.7 to 5.7, indicating that acetone might pose non-carcinogenic threats to the people based on the assessment standard (Ramirez et al., 2012). Meanwhile, in both N_2 +Xe and N_2 +O₂+Xe systems, the HRs of o-xylene (10.9 and 15.3) from m-xylene, m-xylene (23.6 and 92.1) and isopropyl benzene (3.9 and 5.5) from o-xylene, and o-xylene (10.3 and 27.8) and benzene (8.4 and 16.3) from p-xylene were found exceeding 1, and these products also might pose noncarcinogenic threats to the people. The much higher HRs in N_2+Xe system than in N_2+O_2+Xe indicated that oxidation of these products by O₂ efficiently reduces their noncarcinogenic risks.

Similar reduction of non-carcinogenic risk of main products was also observed in N₂+UV (or N₂+VUV) system than in N₂+O₂+UV (or N₂+O₂+VUV) system. It was also found that the HRs of main products of xylenes followed the orders of Xe < UV < VUV in same reaction atmosphere. For example, the HRs of m-xylene obtained from o-xylene photodegradation were 23.6, 44.0 and 105.5 in N₂+O₂+Xe, N₂+O₂+UV and N₂+O₂+VUV systems, while benzene produced from p-xylene photodegradation showed HR of 16.3, 17.3 and 21.8 in N₂+Xe, N₂+UV and N₂+VUV systems. These results suggested that light with shorter wavelength preferred to produce the intermediates with higher non-carcinogenic risks, due to it's the highest photodegradation performance toward xylenes. More-



Fig. 6 - Non-carcinogenic risk of products under different reaction conditions.



Fig. 7 – Occupational exposure cancer risk of products under different reaction conditions.

over, the HRs of acetone in the studied systems showed the same order of magnitude (from 2.7 to 7.1), indicating that the type of the lamp did not influence the non-carcinogenic risk of this product.

In addition, the occupational exposure cancer risks associated with products from photodegradation of xylenes in different systems were evaluated. Fig. 7 shows that the E_i values of most products from xylenes in N₂+Xe and N₂+Xe system were below 0.1. This suggests that these products at this concentration level pose little cancer threat to the workers during photodegradation of xylenes in Xe system. However, benzene showed the E_i values of 0.3 and 0.1 in N_2 +Xe and N₂+Xe system, suggesting possible adverse occupational exposure cancer risks from benzene. Similar phenomenon was also obtained in UV and VUV systems. Previous studies have also proved that the more benzene was produced during the photocatalytic oxidation of AHs, the greater the risk of toxicity and occupational exposure to cancer was (Dhada et al., 2016; Pei and Leung, 2015; Sun et al., 2010), agreeing with the present results. Further comparison revealed that in all studied systems, benzene displayed much higher occupational exposure cancer risk than photo-isomerization products of xylenes, while the opposite trend was observed in non-carcinogenic risks. These results indicated that different photodegradation products of xylenes might show different health risks and more attentions should be paid on their threat to human beings.

2.6. Comparison of OFP, SOAFP and health risk in different reaction systems

To further understand the contribution difference of photodegradation products of xylenes to atmospheric pollution and human health, the comparison of the OFP concentration, SOAFP concentration and health risk from total products of xylenes in different lamp and atmosphere conditions was conducted. As shown in Fig. 8, in the same lamp and atmosphere condition, o-xylene displayed the highest concentration of OFP and SOAFP as well as non-carcinogenic risk, while p-xylene exhibited higher occupational exposure cancer risk than its isomers. Clearly, the photodegradation of xylenes with different methyl group position produced different concentrated intermediates, which expressed different contributions to formation of O₃, SOA and health threat. Zhang et al. observed different SOA formation from photooxidation of mxylene, o-xylene and p-xylene under NO condition and the



Fig. 8 – Comparison of total OFP, SOAFP, non-carcinogenic risk and occupational exposure risk of products under different reaction conditions.

contributions to SOA formation appeared to depend on the xylene substitution pattern (Zhang et al., 2019), partially supporting the present results.

Moreover, it was noticed that higher concentrations of OFP and SOAFP as well as non-carcinogenic and cancer risks were obtained in N_2 system than N_2+O_2 system for the same xylene. It seemed that the presence of oxygen was conducive to further degradation of xylenes and their photodegradation intermediates, reducing secondary pollution and human health threat, especially in VUV system. This was because that N2+O2+VUV system could produce abundant reactive oxygen species (ROS), which easily oxidized xylenes and their intermediates to CO2 and H2O. Choi et al. reported that the generated ROS such as $O(^{1}D)$, $O(^{3}P)$ and O_{3} from photolyzing O₂ by VUV further oxidized the recalcitrant intermediates (Weon et al., 2019), solidly supporting the hypothesis. Chen et al. found a higher intensity of ROS was obtained in gaseous phase of N₂+O₂+VUV system than N₂+O₂+UV system (Chen et al., 2019), further confirming the above conclusion.

In addition, the comparison of OFP, SOAFP and health risk of the products and the degraded xylenes were investigated (Fig. 8 and Appendix A Fig. S7). For convenience, the results of photodegradation of o-xylene in N₂+O₂+VUV system were taken as an example. The OFP or SOAFP of reacted o-xylene after photodegradation reaction for 120 min were calculated as 6.90 or 4.70 \times 10⁴ µg/m³, which was 61.4 or 71.7 times of the produced intermediates (0.11 and 6.55 \times 10² µg/m³). Meanwhile, the non-carcinogenic and occupational exposure risks of the reacted o-xylene were 9.11 \times 10³ and 1.94, which were 70.7 and 20.5 times of the produced intermediates that the photodegradation technology not only efficiently eliminated the o-xylene, but

also prevent the formation of secondary pollution and health threat from the produced intermediates. For all xylenes in all studied systems, the OFP, SOAFP, non-carcinogenic and occupational exposure risks of the produced intermediates were reduced for at least 13.7, 18.7, 17.2 and 4.5 times comparing with the degraded xylenes. However, the produced intermediates also showed relatively high OFP, SOAFP and health risks, suggesting that the secondary pollution and the adverse health impact caused by the products from photodegradation of xylenes could not be ignored. Therefore, the appropriate utilization of the photodegradation technology for purification of industrial organic waste gas was necessary.

3. Conclusions

In the present study, the photodegradation of xylenes under different reaction conditions was studied. The results showed that the degradation efficiency of o-xylene was the highest among all xylenes under the same conditions, while all xylenes showed the highest photodegradation performance in N2+O2+VUV system. Three kinds of intermediates, aromatics, alkanes and carbonyls, were obateind from photodegradation of xylenes, revealing that xylenes underwent the pathways of photo-isomerization, photodecomposition and photo-oxidation. The isomerized products were found not only domination in the contribution of OFP and SOAFP, but also displaying obvious non-carcinogenic risk. While benzene showed the highest occupational exposure risk. Furthermore, the generated products from photodegradation of xylenes displayed relatively high OFP, SOAFP and health risks, suggesting that the secondary pollution and health risks of photodegradation products of xylenes were non-ignorable, though the photodegradation technology effectively removed xylenes. The findings in this study provide a comprehensive understanding of photodegradation process of xylenes and are helpful for the appropriate application of the photodegradation technology in purification of industrial aromatic hydrocarbons in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.12.034.

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