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Kinetic and mechanism studies of musk tonalide reacted with hydroxyl radical and the risk assessment of degradation products

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ABSTRACT

Tonalide was extensively used as fragrances in various personal care products and recognized as emerging contaminant recently. In this study, the transient reactions of hydrophobic tonalide with hydroxyl radical ($\cdot\text{OH}$), one of highly reactive oxygen species (ROs), was firstly investigated in acetonitrile through direct observation using laser flash photolysis. Two transient intermediates were formed with the peak centered at 360 and 450 nm, and the bimolecular reaction rate constants of tonalide with $\cdot\text{OH}$ were determined in both water and acetonitrile solutions with values of 4.04×10^9 and $1.95 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Then, the photocatalytic experiments in a heterogeneous TiO_2 system were carried out to study the decomposition kinetics of tonalide with $\cdot\text{OH}$, which was confirmed as the dominant ROs in photocatalytic system. Five degradation products were identified with molecule weight of 260, 272 and 274. Finally, the potential risks of reaction products formed through the reactions of tonalide with $\cdot\text{OH}$ were further investigated. It is found that the toxicity towards luminescent bacterium (*Photobacterium phosphoreum*) was not changed so much, and the estrogenic activity increased a little bit during the degradation of tonalide by $\cdot\text{OH}$.

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1. Introduction

Polycyclic musk compounds belong to synthetic musk which were typical ingredient of cosmetic and household commodities, such as perfumes, body lotion, soaps, deodorants, and detergents [1,2]. Although the musk in products was usually below 2% [3], the consumption of fragrant products was very huge all over the world, and the discharging of polycyclic musk through wastewater could raise persistent pollution problems in natural waters. Plenty reports found that polycyclic musk distributed widely in various natural aqueous environment, like sea waters [4], fresh waters [5], sediments [6], as well as the body of aquatic organisms around the world [7]. Moreover, polycyclic musk would not only contaminate the aqueous environment, but also tend to accumulate in the

hydrophobic and non-aqueous phases in nature system, due to the high octanol-water partition coefficients for most species of them [8]. As such, some researchers even suggested using synthetic musk as the anthropogenic markers of domestic wastewater [9].

Furthermore, some negative effects were observed by accumulated polycyclic musk in organisms. For example, in the aspect of plants, polycyclic musk was found to inhibit the seed germination and seedling growth of wheat [10]. As to aqueous organisms, polycyclic musk would affect the heart rate of zebrafish larvae [11], and suppress the juvenile development and arise mortality rate of copepod [12]. At molecular level, the toxic mechanism of polycyclic musk were found to cause estrogenic effects [13], genetic injuries [14], gene expression disturbing [15], as well as the cellular xenobiotic defense system damaging [16]. Therefore, both the persistent existence and potential environmental concerns required the investigations on decomposition characteristics, fate and potential risk of polycyclic musk in nature environment.

In natural aqueous systems, photolysis, especially the indirect photodegradation plays an important role in the decomposition of organic pollutants [17]. Hence, to precisely and comprehensively

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understand and predict the fate of polycyclic musk compounds in nature, the degradation of polycyclic musk during indirect photolysis should also be clearly clarified. The indirect photolysis in nature aqueous environment was mainly initiated by reactive oxygen species (ROSs) [18]. Among the ROSs, hydroxyl radical ($\bullet\text{OH}$) with oxidation-reduction potential up to 2.8 V is considered the most reactive specie, which is able to rapidly decompose the alkane and aromatic organic compounds with constants near molecular diffusion rates [19]. As a typical group of emerging organic pollutants, polycyclic musk was composed of aliphatic structures and a benzene ring, thereby implying that they could also be efficiently degraded by $\bullet\text{OH}$. Though the photochemical degradation of polycyclic musk has been studied in several reports, the engagement of ROSs like $\bullet\text{OH}$ in the reaction was either ignored, or just mentioned without direct evidence [20]. For example, the transient reaction spectra and the precise values of bimolecular reaction rate constants (k) of $\bullet\text{OH}$ reacting with musk were barely discussed [21,22]. Moreover, the studies on the $\bullet\text{OH}$ -based advanced oxidation of polycyclic musk were all performed in aqueous rather than non-aqueous solution [23,24]. As such, it could be largely ignored some important transformation process of polycyclic musk compounds with $\bullet\text{OH}$, since polycyclic musk compounds were tend to accumulate in lipid or organic rich samples in natural aqueous systems, such as sludge, sediments or even fatty tissue of aquatic organisms [7,25]. To model the physicochemical reactions in or on the surface of natural non-aqueous environment, pure organic solvent or compounds with weak polarity and hydrogen bond were always adopted, such as acetonitrile, tetrahydrofuran, wax films and heptane [26–29], and these methods made it more meaningful and appropriately to study the kinetics of $\bullet\text{OH}$ with polycyclic musk in non-aqueous or hydrophobic environmental conditions, where the studies were still limited. Last but not least, though the negative effects of parental compounds have been studied, the potential risks of transformation products resulted from the reactions of polycyclic musk with naturally occurred ROSs such as $\bullet\text{OH}$ have not been well clarified yet.

Hence, an extensively used commercial polycyclic musk compound, tonalide was selected as the typical example of polycyclic musk to study its reactions with $\bullet\text{OH}$. Considering acetonitrile was ideal solvent with the weak polarity, high dissolving capacity towards tonalide and relatively low bimolecular rate constant with $\bullet\text{OH}$ ($3.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [19], we decided to adopt this commonly used organic solution to study the non-aqueous reactions of $\bullet\text{OH}$ with tonalide. Firstly, the transient spectra of $\bullet\text{OH}$ reacting with tonalide was studied in detail in a pure acetonitrile solution, where $\bullet\text{OH}$ was yield by laser flash photolysis of N-hydroxypyridine-2-thione (PSH). Secondly, to fully understand the degradation kinetics of tonalide both in water and non-aqueous environment such as the interior of sediment organic matter, the values of bimolecular rate constant (k) were measured and compared both in aqueous and non-aqueous acetonitrile solutions. Then, the photocatalytic TiO_2 system was used as a model system of $\bullet\text{OH}$ -based degradation, further illustrated the role of $\bullet\text{OH}$ in the tonalide degradation kinetics by several scavenging experiments, and the main degradation products were also determined. Finally, the mixtures of tonalide degradation products were extracted, and the evolution of ecotoxicity and estrogenic activity of tonalide during the degradation by $\bullet\text{OH}$ were evaluated.

2. Experimental section

2.1. Materials

Tonalide (purity $\geq 95\%$) and hexamethylbenzene (HMB, purity $\geq 97\%$) were purchased from Adamas Reagent Ltd, Shanghai,

China. N-hydroxypyridine-2-thione (PSH), *trans*-stilbene (TS) and methyl methacrylate (MMA) were obtained from J&K Chemical Ltd (purity $\geq 99\%$). TiO_2 nanoparticles (Degussa P25, 80% anatase, 20% rutile), nano aluminum oxide (Al_2O_3), HPLC grade acetonitrile, high-purity nitrogen (N_2) as well as other reagents were used as received. Luminescent bacterium (*Photobacterium phosphoreum*) was obtained from the Institute of Soil Science, Chinese Academy of Sciences, China. Estrogenic activity assay kit was from Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China.

2.2. Laser flash photolysis

Laser flash photolysis was carried out using a Nd:YAG laser, and the 355 nm laser pulse with duration of 5 ns was used at the energy of 10–15 mJ per pulse. A xenon lamp was employed as detecting light source, and the laser and analyzing light beam passed perpendicularly through a 1×10 mm slit and then to a $10 \times 10 \times 40$ mm quartz cell for the reaction. The transmitted light entered a monochromator equipped with an R955 photomultiplier. The output signal from the HP54510B digital oscillograph was transferred to a personal computer for further data analysis. All of the measurements were carried out at room temperature (25°C) immediately after the preparation. For laser flash photolysis, all experiments were performed under anaerobic condition achieved by degassing with high-purity N_2 .

2.3. Heterogeneous photocatalysis

Decomposition kinetics of tonalide and characterization of the role of $\bullet\text{OH}$ were performed in constantly-stirred slurry of particular TiO_2 (2.0 g L^{-1}) with $50 \mu\text{M}$ tonalide: 2 mL tonalide stock solution (1.5 mM in acetonitrile) was firstly added into the reactor with 120 mg TiO_2 . Mix the solution homogeneously for 20 min and then evaporate the acetonitrile by N_2 blowing. Finally, 60 mL water was filled, and the heterogeneous aqueous solution was prepared by mix homogeneously for another 20 min. A 300 W high-pressure mercury lamp system with a 340 nm cutoff filter was used as the light source as described elsewhere [30]. The heterogeneous solution (5 mL) was sampled at specific time and extracted by hexane three times (1.0 mL each time). The hexane extracts were then combined and dehydrate with 0.1 g Na_2SO_4 . The concentration of tonalide was measured on a HP-5 column (60 m \times 0.25 mm id, 0.25 μm thickness) by gas chromatography-mass spectrometer (GC-MS, Agilent 6890, Agilent, CA, USA) with mass to charge ratio (m/z) of 243.2. Injection temperature was 260°C . Temperature of column oven was firstly hold on 80°C for 1 min, then increased from 80 to 280°C with a gradient of $10^\circ\text{C min}^{-1}$, and hold 280°C for 1 min.

To identify the main degradation products, $100 \mu\text{M}$ tonalide in 2.0 g L^{-1} heterogeneous TiO_2 were prepared, and the photocatalysis reaction was terminated at 30 min. Sixty milliliters of the heterogeneous solution was extracted by hexane for three times (15 mL each time). The extracted solution was combined and dehydrated with Na_2SO_4 , and then evaporated to about 10 mL with a rotary evaporator. Finally, the extract was concentrated and made up to 1.0 mL by nitrogen blow, and 1.0 μL of the extracted sample was directly analyzed by GC-MS. The conditions for GC-MS operation were the same as kinetic studies described above.

2.4. Scavenging experiments

For laser flash photolysis in acetonitrile, 1 M *t*-butanol was used to quench $\bullet\text{OH}$, and methyl methacrylate (MMA, 1 M) was used to quench both $\bullet\text{OH}$ and 2-pyridylthiyl radical (PyS^\bullet) [26]. For the heterogeneous photocatalysis in aqueous TiO_2 , TiO_2 was replaced

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