



Mechanism for the photocatalytic transformation of *s*-triazine herbicides by $\cdot\text{OH}$ radicals over TiO_2



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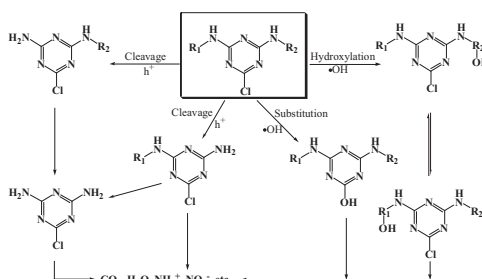
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HIGHLIGHTS

- The degradation kinetics follow the order of *Cya* > *Pro* > *Ter*.
- $\cdot\text{OH}$ radicals have major roles in *Cya*, *Pro* and *Ter* degradation.
- Photohole interaction starts with the *s*-triazine ring.
- $\cdot\text{OH}$ interaction likely to occur at the position next to the Cl group.
- Degradation occurs through cleavage, substitution and hydroxylation pathways.

GRAPHICAL ABSTRACT



Pro: $\text{R}_1 = \text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{CH}_2\text{CH}_2\text{CH}_3$; *Cya*: $\text{R}_1 = \text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{C}(\text{CH}_3)_2\text{CH}_2\text{CN}$; *Ter*: $\text{R}_1 = \text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{C}(\text{CH}_3)_3$

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ABSTRACT

The photocatalytic degradation of *s*-triazine herbicides, viz. propazine (*Pro*), cyanazine (*Cya*) and terbuthylazine (*Ter*), by $\cdot\text{OH}$ radicals over TiO_2 were investigated. The results indicate that all three herbicides were degraded within 90 min, and the rate constants follow the order: *Cya* > *Pro* > *Ter*. The $\cdot\text{OH}$ radicals are heavily involved in the degradation process. It was observed that the adsorption and subsequent reaction of *s*-triazine herbicides with h^+ on the surface of catalyst are significantly subject to the steric-hindrance effect of side chains. Also, there is obvious promotion of degradation rate in the presence of electron-capture agent BrO_3^- . And with the addition of H_2O_2 , there could be promotion as well as suppression of degradation rate across the herbicides. Finally, the point charges, frontier electron densities and reaction energies were analyzed to characterize the adsorption orientation, reaction active sites and reaction direction of *s*-triazine. Based on the calculated data and experimental results, the general degradation pathways are proposed, such as cleavage of side chains, substitution of Cl atom by $\cdot\text{OH}$, and hydroxylation as well as abstraction of hydrogen atoms.

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1. Introduction

The *s*-triazine herbicides are widely used for weed and insect control, and their behaviors in the environment are vitally

important [1–4]. Belong to this group of herbicides are propazine (*Pro*), cyanazine (*Cya*), and terbuthylazine (*Ter*) which are primarily used to control broadleaf weeds [5,6]. They are characterized by a symmetrical six-membered ring with alternating carbon and nitrogen atoms [7,8]. Being water-soluble, and easy to adsorb and hydrolyze, the herbicides cause extensive water and sediment contamination in many countries and regions [9–12]. Despite the use of *s*-triazine as herbicides was banned by the European Union about 15 years ago, there are recent reports of their existence in

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ground waters [13–15]. The presence of *s*-triazine in natural water is a potential threat not only to the ecosystem [16–18], but also human [19–21]. In view of their persistent toxicity, the transformation of *s*-triazine herbicides in the environment is a matter of great concern.

The degradation of organic pollutants in natural water is mainly due their interaction with reactive oxidative species (ROSs) such as $\cdot\text{OH}$, $\text{O}_2\cdot^-$, $\text{CO}_3\cdot^-$, H_2O_2 and $\cdot\text{HO}_2$ [22]. Among them, the $\cdot\text{OH}$ radicals with a redox potential as high as 2.8 V are the most reactive. There are many $\cdot\text{OH}$ -based advanced oxidation processes (AOPs) that were investigated for *s*-triazine degradation, such as O_3 [19,23], Fenton [24–25], UV/TiO₂ [26–30], O_3/TiO_2 [31], pulse radiolysis [32] and electrocatalytic technology [33]. However, most of the studies were focused on removal efficiency, catalytic activity, and synergistic effects of combined methodologies. And the related transformation mechanism and the effect of substituted groups on degradation efficiency are not clear because in each of the cases only one kind of *s*-triazine herbicides was studied [31,34,35]. Furthermore, due to their low concentration in water bodies, the degradation intermediates cannot be fully elucidated by a single modern separation and analytical technique [36], may that be GC/MS or HPLC/MS/MS. Indeed, the knowledge accumulated so far is not adequate enough to establish the general patterns of *s*-triazine degradation. It is hence meaningful to explore new strategies to investigate the transformation pathways of *s*-triazine in the presence of $\cdot\text{OH}$ radicals, especially the common characteristic of transformation pathway and the effects of different substituted groups of *s*-triazine ring on transformation pathway. With the help of these results, the environmental fate, transfer, effect and potential risk of *s*-triazine herbicides can be properly elucidated in environmental waters.

In the present study, the photocatalytic degradation of *s*-triazine herbicides *Pro*, *Cya* and *Ter* with $\cdot\text{OH}$ radicals were investigated. Using purposely designed reaction models, we compared the degradation kinetics, and performed theoretical calculations on point charges (PCs), frontier electron densities (FEDs) and the related energies. Also, the reaction intermediates were identified by a combined use of modern separation and analytical techniques. Based on the experimental and theoretical results, the general pathways for the photocatalytic transformation of *s*-triazine herbicides were proposed.

2. Experimental

2.1. Materials and reagents

Pro, *Cya* and *Ter* (Sigma–Aldrich) were used as received ($\geq 98\%$ purity). Titanium dioxide (P25 TiO₂, Degussa, Germany) was used without pretreatment. HPLC grade water was obtained using a Millipore Milli-Q system which provided constant illumination with a xenon arc lamp at 172 nm to keep total organic carbon concentration of water less than 13 $\mu\text{g}\cdot\text{L}^{-1}$. Acetonitrile and methanol (HPLC grade) were obtained from Sigma. Other reagents were all analytical grade.

2.2. Photocatalytic procedures

The irradiation experiments for degradation study were conducted over a photochemical system (BL-GHX-V, Shanghai Bilon Instrument Company). The Xe lamp (350–780 nm; power consumption 300 W; light intensity 1.28 $\text{mW}\cdot\text{cm}^{-2}$) was positioned 15 cm from the reactor. The adsorption and photocatalytic degradation of *s*-triazine herbicides were carried out in a 150 mL Pyrex reactor with a double-walled cooling-water jacket to maintain constant temperature of solution throughout the experiments.

Prior to illumination, a suspension of 100 μM *s*-triazine and TiO₂ (Degussa P25) of 1.0 g/L concentration was stirred in dark for 30 min to achieve adsorption–desorption equilibrium. Then the Xe lamp was turned on and the solution was constantly stirred. Throughout the photocatalytic degradation experiment, the solution was sampled (2 mL) at fixed time intervals for HPLC and HPLC/MS/MS analysis (after filtration, 0.22 μm Millipore filters). All experiments were performed at room temperature and the pH value of solution was not adjusted. Each batch of experiments was performed in triplicate, and experimental uncertainty in most cases was less than 5%. The sample for GC/MS detection was obtained according to the following procedures: The catalyst was separated (by filtration) upon completion of reaction. And 3 \times 50 mL CH₂Cl₂ was added to the filtrate. The combined organic phase was dried over Na₂SO₄ and subject to filtration and subsequent desolution in ambient conditions.

2.3. Analysis

The analyses of photocatalytic degradation kinetics were carried out at 25 °C using a Cometro 6000 HPLC (Kromasil C18 column, 150 \times 4.6 mm i.d.). The mobile phase was 80% CH₃CN and 20% H₂O for *Pro*, 70% CH₃CN and 30% H₂O for *Cya*, and 55% CH₃CN and 45% H₂O for *Ter*. All of the solutions were filtered with a Water Associates (Milford; MA, USA) 0.45 μm filter. The detection wavelengths for all compounds were 230 nm, and the flow rate of mobile phase was set at 1 mL/min.

The photocatalytic degradation intermediates were analyzed over an HPLC/MS/MS Shimadzu system with Kromasil C18 column (150 \times 4.6 mm i.d.), SIL-HT autosampler, LC-10 AT vacuum pump and API 3000 mass analyzer. The HPLC separations were performed at 0.5 mL/min, with the mobile phases being 20% CH₃CN and 80% H₂O for *Pro*, 30% CH₃CN and 70% H₂O for *Cya*, and 10% CH₃CN and 90% H₂O for *Ter*. An electrospray interface was used for MS and MS–MS measurements in positive ionization mode, and scan acquisition was between *m/z* 50 and 350. The collision energy was varied according to requirement. The other operation parameters were electrospray ionization (ESI) 5.5 keV, source block and desolvation temperature 130 and 400 °C, respectively, nebulizer gas (N₂) flow rate 6 L/min, and argon pressure for collision 250 kPa.

The photocatalytic degradation intermediates were identified by using a Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer equipped with a Varian fused-silica capillary column VF-5 ms coated with 5% diphenylmethylsiloxane (30 m \times 0.25 mm ID, 0.25 μm thickness). High-purity helium (99.999%) at a constant flow rate of 1.5 mL/min was the carrier gas. An AOC-20 auto injector was used for injection (1 μL) at 275 °C in the splitless mode with 1.0 min purge-off time. The temperature program for analysis: 60 °C for 2 min, then heated at a rate of 10 °C/min to 200 °C and held at this temperature for 1 min, and then heated again to 275 °C at the same rate and held at 275 °C for 10 min. The temperature for direct GC interface with the quadruple mass spectrometer was 250 °C, and the electron impact voltage for ionization was 70 eV. The positive fragment ions were analyzed within the 43–500 *m/z* range in SCAN mode with the transfer line and source set at 275 and 200 °C, respectively. Through comparison with the comprehensive data of mass-spectral libraries (such as NIST and Wiley for pesticides), the target compounds were identified unequivocally.

2.4. PCs, FEDs and energies calculation

Molecular orbital calculations were performed using Gaussian 03 program (Gaussian, Inc.) at the single determinant (HF/3-21) level. The optimal conformation having a minimum energy was

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