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Theoretical and experimental insights into the ·OH-mediated mineralization mechanism of flutriafol

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ABSTRACT

Flutriafol is one of the widely used triazole fungicides in global pesticides market, and its degradation mechanisms are important to develop powerful technologies to remove it. Insight into the kinetics and mechanisms of ·OH-mediated mineralization of flutriafol have been obtained using quantum chemical calculation and electrochemical experiment methods. The complete ·OH-mediated degradation pathway of flutriafol was proposed by density functional theory (DFT) simulation and the potential energy surface was mapped out for possible reactions. On the basis of DFT calculations, the optimal ·OH-mediated mineralization mechanism of flutriafol was revealed, and a series of intermediates were observed accumulated in the degradation process, most significance among which were (2-fluorophenyl) (4-fluorophenyl)-Methanone, phenol, dihydroxybenzenes, benzoquinones, muconic acids, maleic acids, oxalic acids and formic acid. To give deeper insight into the ·OH-mediated reaction mechanism, the electrostatic potential (ESP) and average local ionization energy (ALIE) analysis were conducted for o-benzoquinone and p-benzoquinone. The proposed mechanism was further validated by electrochemical experiments at TiO_2-NTs/SnO_2-Sb/PbO_2 anode. The main intermediates were identified and quantified by experimental method, indicating that the proposed ·OH-mediated degradation mechanism derived from DFT calculations was feasible. These detailed findings could be instrumental for a comprehensive understanding of the ·OH-mediated mineralization mechanism of flutriafol and the similar contaminants.

1. Introduction

Flutriafol (FTF), as one of the commercial triazole fungicides, have attracted considerable attention due to their acute toxicity, bioaccumulation and extremely persistent residues in water and soil.[1,2] FTF products with their elevated fungicide activity have attained an important position in the global pesticides market, where the compounds have proved effective in controlling a vast number of diseases affecting diverse fruits, woods and cereal crops.[2–4] However, the extensive use of FTF has resulted in widespread ecotoxicological risk to biological matrices and aquatic ecosystem, promoting the development and implementation of powerful treatment technologies to remove these contaminants.

In recent years, oxidative electrochemical technologies have become attractive alternatives to various conventional environmental remediations, because of their great potential to oxidize, partially or totally, numerous organic compounds.[5–7] Electrochemical oxidation process is based primarily on the intermediacy of hydroxyl radicals (·OH) in the mechanism, resulting in the destruction of most organics.[8] ·OH-induced reactions are mainly responsible for the degradation of contaminants in electrochemical oxidation process, they are also the most complex part of the kinetic mechanism and involve several reaction steps.[9,10] According to previous studies, ·OH can oxidize organic compounds in aqueous medium via three possible mechanisms, eg., ·OH addition to unsaturated bond gives rise to the radical adduct formation (RAF, eq 1); hydrogen atom abstraction by ·OH (HAT, eq 2); and single electron transfer with ·OH (SET, eq 3).[11–13]

$$\text{RAF: } A + \cdot OH \rightarrow \cdot AOH \quad (1)$$

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$$HAT: A + \cdot OH \rightarrow \cdot A(-H) + H_2O \quad (2)$$

$$SET: A + \cdot OH \rightarrow A^{\cdot +} + OH^- \quad (3)$$

Due to the high cost of energy consumption, electrochemical oxidation process has been mostly applied as the pretreatment stage to reduce the effluent toxicity for further treatment.[14,15] It is very important to fully understand the fate of contaminants in aquatic environment, because some of their intermediates might be more environmentally toxic and hazardous than the initial compounds.[10,16–18] Especially, it is appreciated that a comprehensive and deep understanding of the ·OH-mediated degradation mechanism for contaminants, including the detailed transformation byproducts, should be instrumental for effectively improving the application of electrochemical oxidation process in environmental remediation.

Because the whole process of degradation of triazole fungicide is quite complex, only few studies have focused on the degradation mechanism for these contaminants. Ghauch[2] developed a zero-valent iron (ZVI) treatment technology to treat FTF effluent and investigated merely a few intermediates. Han et al.[19] explored the electrochemical degradation of three triazole pesticides (tricyclazole, 1H-1,2,4-triazole and propiconazole) and predicted the active sites of these compounds. The investigations mentioned above unquestionably provide precious information on the degradation mechanisms of triazole fungicides. Nevertheless, limitations still exist in terms of detailed knowledge about the reaction schemes, especially for the evolution of intermediates, because the complexity of the intermediates structure makes it difficult to experimentally investigate the degradation mechanisms.

Quantum chemical calculation has proven to be a powerful tool to obtain deeper insight into reaction mechanisms, as well as offer a very valuable complement to experimental studies.[20–23] Recently, Niu et al.[24] investigated the different roles of ·OH, O_2 and H_2O in electrochemical mineralization of perfluorooctanoic acid (PFOA) using density functional theory (DFT) simulation, and provided insightful explanation for the reaction pathway. However, the FTF is comprised of benzene ring and nitrogen heterocyclic, whose reaction mechanism should be different from that of alkanoic acid.

In this study, quantum mechanical calculations, in combination with the electrochemical experiments, were employed to elucidate the ·OH-mediated mechanisms of degradation of FTF in detail. The possible pathways involved in the reactions of ·OH with FTF were discussed, and the favorable reaction channels were revealed. Furthermore, the topological analysis was conducted to give deeper insight into the mechanisms of ·OH with o-benzoquinone (oBQ) and p-benzoquinone(pBQ), with a special interest into the reactive sites and kinetics for the reactions. Additionally, the intermediates formed in the electrolysis were identified and quantified to verify the theoretical results. At last, a complete ·OH-mediated mineralization pathway of FTF was presented by combining theoretical and experimental analysis. To our knowledge, this is the first time to elucidate the ·OH-mediated mineralization mechanism of FTF by quantum chemical calculation combining with experimental results.

2. Theoretical and experimental methods

2.1. Computational methods

The geometric optimization and vibrational frequencies of all stationary points (including reactants, transition states and intermediates) on the reaction potential energy surface were calculated at the MPWB1K method with 6-311 + G(d,p) basis set [25–27], in the framework of DFT using Gaussian09 programs[28]. The MPWB1K method is a hybrid density functional theory model, which are considered to yield reasonably thermochemical kinetics, weak interaction, hydrogen bonding, and vibrational frequencies.[24,29,30] Moreover, the reliability of the MPWB1K method for organics has been validated by previous studies,[31,32] which reported the available experimental data with the computational results. The solvent effect was also considered by single-point calculations using the conductive polarizable continuum model (CPCM).[33,34] For the potential energy surface we have ensured that every transition state has only one imaginary frequency and verified to connect the reactants and products by performing intrinsic reaction coordinate (IRC) calculations.[35] Moreover, the zero-point energies (ZPEs) were also derived for each stationary point. In this study, TS and IM represent the transition state and the intermediates, respectively.

The parameter ΔE_a represents ZPE corrected activation barrier, which is the difference between energy of TS and those of the reactants. The parameter ΔE_r stands for reaction enthalpies, which is the difference between the energies of the products and those of the reactants. In addition, the activation barrier involving single-electron transfer was calculated using Macurs theory,[36,37] for detail see Text S1 of the Supplementary data.

2.2. Materials and preparation of TiO_2-NTs/SnO_2-Sb/PbO_2 anode

All chemicals in the experiments were of analytical grade and purchased from Aladdin Industrial Corporation, Shanghai, China. Milli-Q water was prepared by Millipore with conductance of 18.2 MΩ cm and used in all the experiments.

In this work, ·OH was produced by electrolysis using TiO_2-NTs/SnO_2-Sb/PbO_2 anode, which have high oxygen evolution overpotential and can generate a large amount of ·OH.[38,39] A typical preparation process of TiO_2-NTs/SnO_2-Sb/PbO_2 anode is described in Text S2.

2.3. Electrochemical experiments

Bulk oxidation of FTF was performed in an electrochemical cell containing 1L FTF solution with 5 g L^{-1} Na_2SO_4 as supporting electrolyte under galvanostatic condition (15 mA cm^{-2}) at 25 °C. Two parallel electrodes (TiO_2-NTs/SnO_2-Sb/PbO_2 as anode and stainless steel sheet as cathode) were set to away from 10 mm. The solution was stirred by magnetic stirring bar in the electrolysis process (for details, see Fig. S1). Samples were collected from the cell at every 15 min for chemical analysis.

2.4. Instrumental analysis.

The concentrations of FTF and its intermediates were measured by high performance liquid chromatography (HPLC-UV, Waters e2695) equipped with a Boston ODS column (5 μm, 4.6 mm × 250 mm). The mobile phase contained a mixture of methanol and water with a rate of 1 mL min^{-1}, and the methanol: water (volume ratio) was 70: 30. Injection volume was 10 μL, the wavelength of ultraviolet (UV) detector was 262.7 nm and 254 nm for FTF and its intermediates, respectively. The residual total organic carbon (TOC) concentrations were measured using a Germany Elementar vario TOC analyzer.

The oxidation intermediates of FTF were identified by gas chromatography-mass spectrometry (GC-MS). The GC-MS system consisted of a GC system (Agilent 7890A) and a MS