



Mechanochemical formation of chlorinated phenoxy radicals and their roles in the remediation of hexachlorobenzene contaminated soil



Shanshan Deng^{a,b}, Nannan Feng^{a,b}, Shaoguo Kang^c, Jianxin Zhu^{a,b,*}, Bo Yu^d, Jing Chen^d, Xiaofeng Xie^d

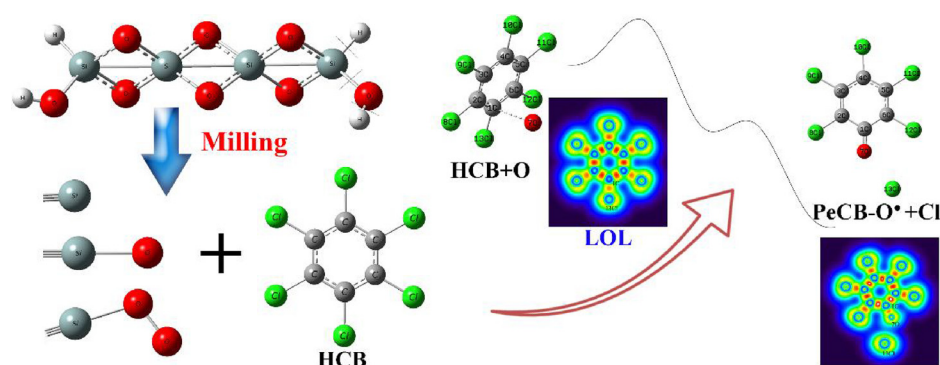
^a Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Yunnan Institute of Environmental Science, Kunming 650034, China

^d Institute of Nuclear and New Energy Technology, Tsinghua University, Haidian District, Beijing 100084, China

GRAPHICAL ABSTRACT



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ABSTRACT

Mechanochemical degradation (MCD) is a promising eco-friendly method to dispose persistent organic pollutants (POPs). Mechanically induced free-radical attack was thought to be one of the key elements in initiating and accelerating the dechlorination and degradation of POPs. In this study, mechanochemical formation of free-radicals and their roles in the remediation of hexachlorobenzene (HCB) contaminated soil were explored using both of experimental analysis and quantum chemical calculations. It was found that chlorinated phenoxy radicals (CB-O•) can be produced in the milling process and they played a vital role in the dechlorination of HCB, based on the results of electron spin-resonance (ESR) and X-ray photoelectron spectra (XPS). Two transition states of mechanochemical reaction along the formation of pentachlorinated phenoxy radical (PeCB-O•) were located, with the energy barriers of 39.4 and 3.4 kJ/mol. The localized orbital locator (LOL), Mayer bond order and topological analysis were also implemented to depict the process in detail. Free-radical attack dominated dechlorination pathway of HCB in the MCD process was also verified by the Fukui function analysis. The study on the mechanically-induced generation of free-radicals and their associated modes of action on the degradation of HCB will provide a deep insight into mechanochemical remediation mechanism of POPs contaminated soil.

* Corresponding author at: Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China.
E-mail address: zhujx@rcees.ac.cn (J. Zhu).

1. Introduction

Persistent organic pollutants (POPs) contaminated soil remediation is a global challenge because these contaminants are refractory, semi-volatile, dispersive, biological toxic and bio-accumulative [1–3], which can re-enter the air, water, plants, animals and human bodies without a safe disposal [4–6]. Recently, mechanochemical degradation (MCD) has been viewed as an eco-friendly method for the disposal of POPs and other emerging pollutants [7,8], due to its main advantages: non-combustion, solvent-free, less CO₂ and hazardous byproducts emissions etc. [8–10]. MCD couples the mechanical and chemical modes of action, which can trigger chemical reactions by mechanical force, such as shear, friction, shock and squeeze [9–11]. The mechanical force can induce solid structure transformations and promote solid-solid or solid-liquid interactions, allowing the targeted contaminates to be completely dechlorinated and destructed at modest temperatures and pressures [12,13].

Mechanism clarification for mechanochemical dechlorination is of great importance because the number of chlorine substituents and their distribution on the phenyl ring exert a tremendous influence on their toxicity. Some researchers found that the mechanical force would bring about release of electrons, rupture of chemical bonds and formation of radicals, which have a close relationship with degradation efficiency [14–17]. Co-milling reagents can be mainly classified into four groups: Lewis bases, reductants, oxidants and neutral reagents, each type has a peculiar electron transfer mechanism that determines diversity of the mechanochemical reaction routes [8]. Lewis base can induce the electron transfer from oxide ions to organics and form the anion radical or free radical under the mechanical energy. Reductants can be functioned as the electron and hydrogen donors, and oxidants can oxidize organic pollutants to radicals and cations. Neutral species can also generate highly active free radicals or fracture-surfaces with oxidizing centers during milling. Moreover, the reactivity of metal oxides is also determined by trapped electrons on particle surfaces, which are generated by oxygen vacancy formation on the surface lattice [18]. The formation of oxygen-centered aromatic radicals (Ar-O·) was found to play a vital role in the MCD of POPs [18–21]. Ikoma and Tanaka et al. verified the generation of Ar-O· and their vital roles in the MCD of 3-chlorobiphenyl (BP-Cl) using CaO as co-milling reagents [18,20]. The oxygenated radicals were also proposed as the MCD intermediates of perfluorinated pollutants [21]. It was generally agreed that the MCD process consisted mainly of the dehalogenation, ring cleavage and polymerization mechanisms [22–24]. However, the formation mechanism of Ar-O· radicals as well as their roles to determine the dechlorination pathway and distribution of intermediate products still remain a steep challenge for lack of effective in-situ detection methods in a milling jar.

Quantum chemical calculations combined with equipment analysis might provide a salient insight into the MCD mechanism perspicuity, which were recently employed to confirm the mechanism of organics degradation [25–27]. Density functional theory (DFT) was especially used to propose and validate the reaction pathways of BDE 209 and associated oxidative products [28]. It is also a powerful tool for the transition state theory to reveal the reaction route and active energy theoretically [29,30]. Hexachlorobenzene (HCB) can be an excellent surrogate of polychlorinated biphenyls, polybromodiphenyl ether, and hexabromocyclododecane in the contaminated soils remediation [31]. Our previous work confirmed the dominance of chlorinated phenoxy radicals (CB-O·) in the MCD of HCB using alumina as the co-milling reagent [32]. Obviously, more works are needed to shed light on the CB-O· in more detail.

The present study extended investigations into the formation mechanism of CB-O· as well as their roles in the dechlorination reactions by both of experimental and theoretical analysis. Formation of CB-O· was verified by the distribution of low-chlorinated intermediate products, electron spin-resonance (ESR) and X-ray photoelectron spectra

(XPS). We utilized the hybrid B3LYP method to simulate the major mechanochemical formation pathway of CB-O· radicals. The bonding evolution of the dechlorination pathway was investigated by diverse methods, including localized orbital locator (LOL), Mayer bond order (MBO) [33] and topological analysis [34]. Moreover, the degradation pathway of HCB induced by CB-O· was analyzed by Fukui function [35]. The study on the formation of CB-O· and their roles will provide a deep insight into the mechanochemical remediation of POPs contaminated soil.

2. Materials and methods

2.1. Samples and chemicals

Hexachlorobenzene (HCB, purity 99%) used in the mechanochemical reaction was purchased from Beijing HWRK Chem Co., Ltd. Detailed list of other reagents and solvents were shown in Table S1 in the supplementary material (SM).

Two types of natural and two types of synthesized soil samples were utilized in the present study. The natural soil samples were from Zhuzhou City, Hunan province (hereafter as ZZS) and Dayu City, Jiangxi province (DYS). The major contents of ZZS and DHS were measured by X-ray fluorescence spectrometer (XRF-1700, Shimadzu, Japan) and shown in Table 1. Two synthesized soil samples were synthetic sandy base soil (SBS) and Fe/Mn-riched sandy soil (SOS), as shown in Table 1 [36]. With regard to the HCB contaminated soil, we added a small amount of soil into the HCB/hexane solution, stirred it thoroughly to ensure uniformity, then evaporated the hexane to get the wanted sample. Since HCB attachment ability varies largely for different soil samples, the final HCB concentration in each kind of soil sample were measured three times by Gas Chromatography-Mass spectrometer (GC-MS) [37]. Average HCB concentrations in ZZS, DHS, SBS and SOS soil samples were 644, 783, 555, and 555 mg/kg, respectively.

2.2. MCD experiments

MCD experiments of HCB contaminated soils were conducted in a QM-3SP2 planetary ball mill made by Nanjing University Instrument Corporation, China. 0.6 g mixture of soil and co-milling agents was placed into a 250 mL steel pot with 180 g stainless balls. The ball-to-powder weight ratio was 30:1 and the rotation speed was set at 550 rpm. 0.5% and 1% mass ratio of HA were added to investigate its impact on degradation rates. The milling time was set 30 min, 60 min, 90 min, 120 min, 150 min, 180 min and 210 min. After milling, residues were collected and preserved in a close dryer for further analysis.

Table 1

Main composition of soil samples used in the mechanochemical degradation of hexachlorobenzene (%wt.).

Reagent /%wt	ZZS	DYS	SBS ¹	SOS ¹
SiO ₂	70.85	65.85	83.67	81.67
Al ₂ O ₃	15.58	19.58	5.67	5.67
Fe ₂ O ₃	7.24	7.64	0.25	1.50
K ₂ O	2.92	3.98	–	–
TiO ₂	1.42	1.21	–	–
Mn ₂ O ₃	–	–	0.25	1.50
CaCO ₃	–	–	0.50	0.50
Humic acid	–	–	1.00	1.00

¹ Bentonite (Al₂O₃·4(SiO₂)·H₂O) were used instead of the pure Al₂O₃ for the synthesized soils and contention of SiO₂ were converted based on the chemical formula.

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