



Study of degradation mechanism of dechlorane plus by mechanochemical reaction with aluminum and quartz sand

Haizhu Wang^{a,b}, Jun Huang^{a,*}, Siyu Zhang^a, Ying Xu^c, Kunlun Zhang^a, Kai Liu^a, Zhiguo Cao^a, Gang Yu^a, Shubo Deng^a, Yujue Wang^a, Bin Wang^a

^aState Key Joint Laboratory of Environment Simulation and Pollution Control (SKJLESPEC), Beijing Key Laboratory for Emerging Organic Contaminants Control, School of Environment, POPs Research Center, Tsinghua University, Beijing 100084, PR China

^bState Key Laboratory of High Power Semiconductor Laser, Changchun University of Science and Technology, Changchun 130022, PR China

^cSchool of Physics, Northeast Normal University, Changchun 130024, PR China

HIGHLIGHTS

- Mechanochemical destruction of DP was prompted by Al and quartz sand.
- Main solid products include carbon, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, silicon etc.
- Main gaseous products include H_2 , CH_4 , C_2H_6 , C_2H_4 etc.
- Thermite-type reaction and dechlorination followed by carbonization are mechanism.

ARTICLE INFO

Article history:

Received 25 November 2015

Received in revised form 30 January 2016

Accepted 5 February 2016

Available online 9 February 2016

Keywords:

Mechanochemical destruction
Dechlorane plus
Quantum chemical calculations
Thermite-type reaction

ABSTRACT

Mechanical force, which directly induced specific chemical reaction by the collision between balls or ball and vial, have recently attracted much attention on efficient and rapid destruction of organic pollutants. To exploit this mechanochemical destruction (MCD) technology, it is essential to develop a fundamental understanding of the mechanism of degradation contaminant. Here we report a detailed study on the MCD of the additive flame retardant of dechlorane plus (DP), using Al and quartz sand (SiO_2) as additives. Degradation data and quantum chemical calculations based on density functional theory (DFT) confirmed that the different mechanism of MCD for treatment of different mass ratio of DP in the mixture of Al + SiO_2 . The intermediate products of DP's' ($\text{C}_{18}\text{H}_{13}\text{Cl}_{11}$) and DP's'' ($\text{C}_{18}\text{H}_{14}\text{Cl}_{10}$) were observed in the low mass ratio. Sequential dechlorination followed by the destruction of hydrocarbon skeleton should be the main degradation pathway of low mass ratio of DP. Moreover, mechanically induced thermite-type reaction is responsible for the more efficient destruction of high mass ratio of DP. The potential fate of C and Cl present in DP was in the form of amorphous and graphite carbon, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and certain polymerized with Si–Cl bonds, respectively. The H present in DP was mainly contained in the final gas products H_2 , CH_4 , C_2H_6 , C_2H_4 etc. This study paves the way toward the efficient and rapid destruction of toxic chlorinated organic pollutants like DP using MCD.

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1. Introduction

Mechanochemistry is concerned with chemical transformation induced by mechanical means, typically by means of high-energy ball milling [1]. During the ball milling process, unintentional chemical reaction can be applied to prepare useful new materials and improve the efficiency of complex processes.

In 1994, Rowlands et al. first introduced mechanochemistry into the environmental field to destruct persistent organic pollutants (POPs). It is first reported that dichlorodiphenyltrichloroethane (DDT) can be completely degraded using mechanochemical method with calcium oxide (CaO), by which DDT was transformed into CaCl_2 and graphite after 12 h ball milling [2]. Since then, MCD as a non-combustion alternative for the destruction of organohalogen materials has received great interests. And CaO as additive have been widely applied for MCD of various POPs.

* Corresponding author. Tel.: +86 10 62792598; fax: +86 10 62794006.

E-mail address: huangjun@tsinghua.edu.cn (J. Huang).

Subsequent research further supported the feasibility of using mechanochemical treatment of POPs with a planetary ball mill. Various oxides additives successfully degraded certain POPs via MCD, such as trichlorobenzene [3], octachlorinated dibenzodioxin and furan [4], pentachlorophenol [5], phenanthrene [6], pentachlorophenol [7], etc., with final products achieved carbonization. By mixing quartz sand (SiO_2) with CaO and zero-valent metals as additives, the degradation efficiency of POPs, such as 3-chlorobiphenyl [8], organobromine tetrabromobisphenol A (TBBPA) [9] and organochlorine mirex [10], were greatly enhanced. However, these results achieved at low mass ratio of POPs, with no reasonable explanation to the degradation mechanism. In addition, low mass ratio results in lower POPs destruction efficiency at industrial scale, which hinders the practical application of MCD.

Recently, the solid-state reaction between chlorinated flame retardant DP and Al + SiO_2 was investigated, and DP has achieved environmentally sound destruction by mechanochemical method [11]. But it is worthy of further interest in the disposal of chlorinated POPs. Particularly highly reductive Al may induce self-propagating reaction under different stoichiometry of the reacting mixture. In fact, mechanically induced self-propagating reactions (MSR) have been observed in a variety of systems [12], and accompanied combustion-like phenomenon is observed during milling. However, to the best of our knowledge, few literatures reported combustion-like reaction which involves organic compounds [13]. Consequently, the study of DP degradation using MSR with co-grinding Al and SiO_2 may greatly promote degradation efficiency.

In this paper, a combination of Al + SiO_2 was investigated for the effect of self-propagating reaction on MCD of technical DP with different mass ratio in a planetary ball mill. The final solid and gaseous products were analyzed, and the potential fate of H, C, and Cl present in DP was elucidated based on chemical analysis, surface characterization and on-line mass spectrogram (on-line MS). Both dechlorination process and degradation mechanism are discussed.

2. Materials and methods

2.1. Materials

A technical DP product ($\text{C}_{18}\text{H}_{12}\text{Cl}_{12}$, 99% in purity) was purchased from Jiangsu Anpon Electrochemical (China). The percentage of *anti*-DP and *syn*-DP is 75% and 25%, respectively. Aluminum powder (Al \geq 98% in purity, 300 mesh in size), and quartz sand (SiO_2 , \geq 99.8% in purity) were obtained from Sinopharm Chemical Reagent (China). All solvents (methanol and hexane) used for extraction and clean-up were of HPLC grade or higher (J.T. Baker, USA). All chemicals were used as received.

2.2. Mechanochemical process

A planetary ball mill (QM-3SP2, Nanjing University Instrument, China) was used in the experiments. 80 mL stainless vial was filled with stainless balls with diameter between 5 and 10 mm, which serve as the milling medium. The balls filling ratio reach about one third of stainless vial, and the weight ratio between 5 and 10 mm balls is 1:2. Al and SiO_2 were added as additives during ball milling of DPs. The experimental parameters of Al/ SiO_2 molar ratio and charge ratio (C_R) were fixed at 5:1 and 20:1, respectively. Where the $C_R = m_b/m_p$ is considered to be an important factor of MCD efficiency, m_b is the total mass of the balls and m_p is the total mass of DP and the Al + SiO_2 additives. Because these factors have been discussed in the previous article, the effect of the mass ratio

of DPs in the mixture was discussed in detail (the mass ratio of DPs is the mass percent of DPs in the mixture) in this paper. The mixture was placed in the covered stainless vial containing balls in ambient air condition and placed inside the planetary ball mill, which was operated at a rotary speed of 275 rpm and the rotation direction changed automatically every 30 min.

2.3. Sample analysis

0.01 g different mass ratio of milled mixture was ultrasonically extracted with hexane, and centrifugalized at 3000 rpm for 15 min to remove solids from the extraction. DPs were analyzed using an Agilent 6890 plus gas chromatography equipped with a microelectron capture detector (GC/ μ ECD; Agilent, USA) and a DB-5MS capillary column (30 m \times 0.25 mm \times 0.25 μm). Nitrogen (99.999% in purity) was used as carrier gas at a constant flow of 34.5 mL/min. GC oven temperature was programmed from 140 $^\circ\text{C}$ (held for 1 min) to 250 $^\circ\text{C}$ at 30 $^\circ\text{C}/\text{min}$, and to a final temperature of 285 $^\circ\text{C}$ at 0.8 $^\circ\text{C}/\text{min}$ (held for 5 min).

0.15 g different mass ratio of 2 h-milled mixture was extracted as the same way with hexane. DPs and possible degradation products were analyzed using a gas chromatography/mass spectrometry (Shimadzu GC/MS-QP 2010 Plus, Kyoto, Japan), equipped with a DB-5MS capillary column (15 m \times 0.25 mm i.d., 0.10 μm film thickness). Helium (99.999% purity) was used as carrier gas at a constant linear velocity of 75.7 cm/s. GC oven temperature was programmed from 60 (held for 1 min) to 230 $^\circ\text{C}$ at 40 $^\circ\text{C}/\text{min}$, from 230 to 240 $^\circ\text{C}$ at 1 $^\circ\text{C}/\text{min}$, to 260 $^\circ\text{C}$ at 0.5 $^\circ\text{C}/\text{min}$, and to a final temperature of 280 $^\circ\text{C}$ at 2 $^\circ\text{C}/\text{min}$. The mass spectrometer was operated in NCI mode, the temperature of the ion source and interface were set at 200 and 280 $^\circ\text{C}$. However, the milled mixture with mass ratio of 25%, 33%, and 50% did not detect signals, the measurement result of mass ratio 17% was completely similar to mass ratio 8%, the mass ratio 8% was selected as example for understanding the degradation intermediates and pathway.

0.02 g mixture with mass ratio of 50% was taken for the determination of water soluble chloride. The mixture was ultrasonically agitated in 50 mL deionized water at 60 $^\circ\text{C}$ for 30 min, and centrifugalized at 3000 rpm for 15 min. The separated solid residue was extracted twice for inorganic content the Cl ions. The combined solution was concentrated using gentle nitrogen flow and analyzed for chloride ions by a DX-1000 ion chromatography (IC) (Dionex, USA) equipped with an Ion-Pac AS4A-SC anion exchange column. The vial temperature was measured by surface temperature indicating strips, which the initial measurement temperature was 40 $^\circ\text{C}$, and the test temperature was irreversible.

2.4. Identification of final products

The final products were identified by X-ray Powder Diffraction (XRD, Rigaku D/max-r B, Japan) using the following settings: Gu $K\alpha$ radiation, 40 keV accelerating voltage, 80 mA current, 10–90 $^\circ$ 2θ scanning range, 0.02 $^\circ$ step and 6 $^\circ/\text{min}$ scan speed. The composition of final products was detected by X-ray Photoelectron Spectrometry (XPS) (Thermo SCIENTIFIC ESCALAB 250Xi) with Al $K\alpha$ X-ray source. The binding energy scale was calibrated by C_{1s} peak of 284.8 eV in XPS measurement. Raman spectra were recorded at room temperature using a Microscopic Confocal Raman Spectrometer (Renishaw RM 2000, UK) with Ar-laser beam at the 514.5 nm line. The final gaseous products were performed with a mass spectrometer (Thermostat GSD 320) operating in residual gas analyzer mode, and the whole system is purged with ultra-high purity Ar to ensure baseline level.

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