Mechanochemical mechanism of rapid dechlorination of hexachlorobenzene

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

^a Department of Solid Waste Treatment and Recycling, 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 BCEG Environmental Remediation Co. Ltd., No. 6 Jingshun East Street, Chaoyang District, Beijing 100015, China

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

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ABSTRACT

Recent researches indicate that mechanochemical treatment (MCT) is a promising method to degrade the environmental hazards, especially in the area of persistent organic pollutants (POPs) disposal. However, the mechanochemical dechlorination mechanism of POPs still needs to be further verified. In this mechanochemical process, hexachlorobenzene (HCB) was chosen as a model pollutant with aluminum and alumina ($\text{Al} + \text{Al}_2\text{O}_3$) powders as the co-milling reagents. Both of the intermediate analysis and quantum chemical calculations were adopted to elucidate the free radical dechlorination mechanism of HCB. The solid residues were characterized by electron spin-resonance (ESR) spectroscopy, Fourier transform infrared (FTIR) spectra and X-ray photoelectron (XPS) spectra, which proposed that the radicals formed in the mechanochemical process were chlorinated phenoxyl radicals ($\text{CB-O}^\bullet$). Four quantum chemical descriptors were selected in predicting the intermediates and reaction pathway: (i) atomic charge, (ii) electrostatic potential (ESP), (iii) frontier molecular orbitals (FMO) theory and (iv) dual descriptor. Then, a stepwise dechlorination mechanism based on $\text{CB-O}^\bullet$ was proposed. It was found that the intermediates and radical-related reactions in the mechanochemical dechlorination of HCB are quite different from that happen in a typical photocatalytic dechlorination process. Impacts of different radical reactions on the dechlorination of HCB were also compared at last.

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1. Introduction

Mechanochemistry is a branch of chemistry [1,2], named to illustrate the chemical and physicochemical transformations of substances triggered by mechanical force, such as shearing, friction, shock and squeeze [3–6]. Mechanochemical method has been widely used in extractive metallurgy [7–9], material synthesis [10,11], powder surface modification [12] and hazards attenuation [13–15]. Compared with conventional procedures, mechanochemical technology has several main advantages: no-combustion, solvent-free, low energy consumption, less CO_2 and hazardous byproducts emissions, possible implementation process etc.

[4,6,16,17]. Therefore, mechanochemical treatment (MCT) has been listed as one of the most promising no-combustion and eco-friendly technologies for the disposal of the persistent organic pollutants (POPs), such as 1,3,5-trichlorobenzene, 3-chlorobiphenyl, 4-chloroaniline, γ -hexachlorocyclohexane, dioxins, mirex, pentachlorophenol and polychlorinated biphenyls [18–24].

It has been proven by plenty of studies that free radical is one of the key elements in the MCT process [25–28], which can induce and accelerate the dechlorination and degradation process. Some investigations demonstrated the formation of triboplasma [25,29]; it has been deemed to be a highly energetic state containing highly ionized gas [30]. The degradation of tetrabromobisphenol A (TBBPA) and HCB through a milling method gave credit to the generation and transportation of radicals [25,27,31]. The relationship between the degradation rates of POPs and the yield of paramagnetic products was also verified in the MCT of mono-chlorobiphenyl [32]. The oxygen-centered aromatic radical ($\text{Ar-O}^\bullet$) was proposed in the MCT of 3-chlorobiphenyl (BP-Cl) and pentachlorophenol [23,26]. How-

* Corresponding author at: Department of Solid Waste Treatment and Recycling, 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).

Fig. 1. Degradation of HCB and formation of low-chlorinated isomers in the MCT process: (a) CBz congeners, (b) TeCBs isomers, (c) TrCBs isomers and (d) DCBs isomers.

ever, the details of this radical-related dechlorination route are hard to obtain from previous studies. Hence, clarification and description of the radical reaction mechanism in the mechanochemical dechlorination process is a steep and urgent challenge for understanding the nature of MCT.

Recently, many researchers used quantum chemical calculation, especially density functional theory (DFT), to investigate the mechanism behind the degradation of organic pollutants [33–35]. Quantum chemical descriptors can be exploited to characterize specific molecular properties and predict active sites of the certain reaction. These descriptors were defined to indicate molecular structure and chemical properties, which have been put into use successfully [36]. This train of thought provides insight into the mechanisms perspicuity that cannot be elucidated solely based on experimental data. Several typical descriptors, such as atomic charge [37], frontier molecular orbital (FMO) theory [38], electrostatic potential (ESP) [39], Fukui function [40] and dual descriptor [41], are entirely based on electronic characteristics of reactants, so most of them are cheap and efficient [42,43]. Moreover, composite of several methods can enhance the reliability of theoretical prediction [44]. Several kinds of descriptors were performed synergistically in some DFT studies [45–47].

As for the reason why Metal/ Al_2O_3 was selected as the co-milling reagent of MCT of HCB, many previous studies demonstrated its effectiveness in the organic pollutants treatment from their excellent adsorption and chemical composition properties [48–52]. HCB was selected as the model pollutant due to its universality, typical symmetry and polysubstitution. The intermediates during the MCT process were analyzed regularly to provide the basic information for the mechanism study. In addition, four quantum chemical

Fig. 2. ESR of initial Al_2O_3 sample (cyan line) and samples grinding 90 min (blue for Al_2O_3 and red line for Al_2O_3 + HCB samples). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

descriptors, atomic charge, ESP, FMO theory and dual descriptor, were employed to predict the active sites and validate the radical reactions expected. Finally, a systematic solid state step-wise dechlorination mechanism in the MCT of HCB was proposed based on both experiments and quantum calculations. Impacts of different radical reactions on the dechlorination of HCB were also compared at last.

Fig. 3. FTIR spectra of ground samples.

2. Materials and methods

2.1. Materials

HCB (purity 99%) was purchased from Beijing HWRK Chem Co., Ltd. CBz standards of chlorobenzene produced by Accu Standard Inc. were used for gas chromatography-mass spectrometry (GC-MS) analysis, including HCB, pentachlorobenzene (PeCB), tetrachlorobenzenes (TeCBs, including 1,2,3,4-TeCB, 1,2,3,5-TeCB and 1,2,4,5-TeCB), trichlorobenzenes (TrCBs, including 1,2,3-TrCB, 1,2,4-TrCB and 1,3,5-TrCB), dichlorobenzenes (DCBs, including 1,2-DCB, 1,3-DCB and 1,4-DCB) and monochlorobenzene (MCB). Anhydrous sodium sulfate (GR, Sino pharm Chemical Reagent Co., Ltd, China) were heated in a muffle furnace at 400 °C for 6 h before using and stored in a dryer prior. The milling additives were aluminum powder (Al, 30 μm grade, Sino pharm Chemical Reagent Co., Ltd, China) and aluminum oxide (Al₂O₃, 300 μm, Sino pharm Chemical Reagent Co., Ltd, China). Normal hexane (Fisher Scientific) and acetone (Fisher Scientific) were at HPLC grade.

2.2. Ball milling experiments

All ball milling experiments were carried out in a planetary ball mill (QM-3SP2J), sold by Nanjing University Instrument Corporation, China. 3 g Al, 3 g Al₂O₃ and 0.3 g HCB were put into a milling pot. Both of the milling pots (250 mL) and balls (about 180 g, Φ10 mm) were made of stainless steel. Milling experiments were operated at a rotation speed of 550 rpm with a charge ratio of 30:1 and additive to HCB mass ratio of 20:1.

2.3. Analytical procedures

The residual HCB and dechlorinated intermediates were detected by chromatography-mass spectrometry (GC-MS, Agilent 7890), and the detailed procedure for sample preparation and detection can be found in the Supplementary Material. Radicals were observed using the electron spin-resonance (ESR) spectroscopy. Samples for ESR analysis were specifically prepared using a zirconia pot (ZrO₂) and balls, eliminating the interference of Fe. After milling for certain times, samples were immediately transferred into the 5 nm diameter quartz tubes to be measured at the X band (9.6 GHz, Bruker ESR-380E). Fourier transformed infrared (FTIR) spectra were detected to determine the functional groups of samples. The apparatus model is Nicolet 6700, made by Thermo-Fisher using KBr disk method with the wave number from 400 to 4000 cm⁻¹. The X-ray photoelectron (XPS) spectra of the O 1s were

Fig. 4. XPS spectra (O 1s) of ground samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

recorded with a step size of 0.05 eV using an ESCALAB 250Xi instrument (Thermal fisher) set at a constant analyzer pass energy of 30.0 eV.

2.4. Degradation pathway analysis by quantum chemical calculation

All calculations of this article were carried on Gaussian 09W [53], and the molecular constructing and visualizing were performed with Gaussian View 5.0.9. Equilibrium geometry optimizations of all structures, followed by frequency calculations were operated by the DFT Becke3LYP (B3LYP) method. B3LYP, the three-parameter hybrid density model, which is the most popular DFT method including a mixture of Hatree-Fock exchange and DFT exchange correlation, has been employed by many quantum calculation processes [54]. Split valance basis sets 6–31G (d) and 6–311G (d) were utilized to the optimizations and single point energy calculations, respectively [55,56]. Gibbs free energies were calculated based on the single point energies and the thermal corrections. Zero-point corrections, thermal corrections and correction factors were all taken into account for the Gibbs free energy change (ΔG) calculations and the Gibbs free energy of free electron was -3.6160 kJ/mol [57]. Calculations for quantum chemical descriptors to predict the reactive site of the radical reactions, including atomic charge, ESP, FMO theory and dual descriptor, were carried out with Multiwfn, the multifunctional wave function analysis [58], and details for these methods can be seen in the Supplementary Material.

3. Results and discussion

3.1. Experimental dechlorination pathways of HCB in the MCT process

The time courses for the dechlorination of HCB and the formation of low-chlorinated isomers in the MCT process are shown in Fig. 1(a–d). After 60 min of milling with Al and Al₂O₃, 99.3% of HCB was degraded in the MCT process with Al and Al₂O₃ as co-milling reagents (see Fig. S1 in Supplementary Material). The role of oxides has been probed in some reports [26]. Gerd Kaupp [59] proposed that mechanical collision and friction can induce the crack of strong covalent bonds and trigger chemical reactions on the surface of oxides. Al₂O₃ in the milling system can also prevent the formation of agglomerates, increase the effective interparticulate contact area and promote mechanochemical reactions [22,26].

The congeners of low-chlorinated isomers in the MCT process detected by GC-MS, including PeCB, TeCBs, TrCBs, DCBs and MCB.

Table 1

Atomic charges of PeCB-O•, 2,3,4,5-TeCB-O•, 3,4,5-TrCB-O• and 3,4-DCB-O• radicals calculated by Mulliken population, Hirshfeld population and MK ESP fitting charge analysis.

Structure	Atom	Mulliken	Hirshfeld	MK ESP
1	0.4415	0.0608	0.3961
	2	-0.1361	0.0017	-0.1588
	3	-0.0897	0.0162	0.1110
	4	-0.0820	0.0029	-0.0382
	5	-0.0897	0.0162	0.1117
	6	-0.1361	0.0017	-0.1605
1	0.4451	0.1055	0.5660
	2	-0.1641	-0.0270	-0.2667
	3	-0.0581	0.0227	0.0454
	4	-0.0829	0.0354	-0.0717
	5	-0.0730	0.0123	0.0527
	6	-0.1395	0.0269	-0.1127
1	0.4280	0.1090	0.5178
	2	-0.1614	-0.0247	-0.2193
	3	-0.0609	0.0237	0.0236
	4	-0.0856	0.0358	0.1150
	5	-0.0609	0.0237	0.0234
	6	-0.1614	-0.0247	-0.2198
1	0.4196	0.0070	0.5480
	2	-0.1538	0.0682	-0.2660
	3	-0.1183	0.0560	-0.0756
	4	-0.0770	0.0651	0.0525
	5	-0.0625	0.0813	0.0871
	6	-0.1665	0.0678	-0.2429

The concentration of MCB was too low to be quantified accurately, so it was not presented in the figures. Fig. 1a shows the contents of PeCB, TeCBs, TrCBs and DCBs in residuals that increase in the first 30 min and then decrease with increment of milling time. It shows that PeCB is the prominent lower-chlorobenzene intermediates through the whole process. Relative concentration changes of the low-chlorinated isomers indicates the stepwise dechlorination pathway.

Fig. 1(b) shows that 1,2,3,4-TeCB is the prominent tetrachlorobenzene intermediate, whose concentration is much higher than the other two isomers, implying that ortho-Cl might be the most preferred position to be removed in the PeCB dechlorination. While, the concentration of 1, 2, 4, 5-TeCB was on the similar level to that of 1, 2, 3, 5-TeCB, indicating similar preference for the dechlorination of PeCB at the sites of meta-Cl and para-Cl. Fig. 1(c) shows that 1,2,3-TrCB and 1,3,5-TrCB are the prominent and unremarkable trichlorobenzene intermediate isomers in the ball milling, respectively. Fig. 1(d) depicts the distribution of DCBs in the milled samples, where, 1, 2-DCB holds the largest concentration among the three kind of dichlorobenzene intermediates. It can be concluded that the main dechlorination pathway for HCB in the MCT process could be depicted as follows: HCB → PeCB → 1,2,3,4-TeCB → 1,2,3-TrCB → 1,2-DCB → MCB.

3.2. Radicals observed in mechanochemical degradation of HCB

Large amounts of free radicals were produced during the milling of Al₂O₃, so ESR was employed to detect the mechano-radicals. This was also reported by Zhang and Huang et al. in the grinding of CaO, SiO₂ and other oxides [27,60]. Fig. 2 shows the ESR spectra of

the original Al₂O₃ powder (cyan curve), Al₂O₃ powder grounded (blue curve) and mixtures of Al₂O₃ + HCB grounded (red curve) for 90 min. Unground Al₂O₃ showed no radical signals, while apparent signals can be seen at around 324 mT in ground samples. The blue curve depicts the signal of milled Al₂O₃, with a sharp signal at $g = 1.980$ and a broad signal at $g = 2.034$. The first one indicates the trapped electron on Al₂O₃ surface, which is smaller than the free electron $g_e = 2.002$. It was reported that lattice surfaces of Al₂O₃, originally terminated with an oxygen layer, would capture hydrogen to neutralize the surface charge, thus the oxygen layer turns into the structure terminated with hydroxyl groups [61,62]. The milling process can destruct hydroxyl layer, lead to deprotonation, induce the release of free electrons and create fresh surface with large amounts of active O²⁻ sites. These electrons and active O²⁻ sites on oxide surfaces could transfer to organic compounds to produce large amounts of radicals under the pressure, collision, extrusion and friction in the MCT process [26,32].

The ESR spectra of the milled Al₂O₃ + HCB sample (red curve) shows two peaks at $g = 1.998$ and 2.109. Similar with the milled Al₂O₃ sample, the first sharp signal indicated trapped electrons on Al₂O₃ surface. The last broad signal was slightly deviated and enhanced compared to the milled Al₂O₃ sample, implying that addition of organic matters changed the structures and species of radicals. The radicals might be the chlorinated phenoxy radicals (CB-O•), which was the resultant of reactions between HCB and trapped electrons or O²⁻ on the surface of the milled Al₂O₃ particles. The oxygen-centered aromatic radicals were also observed and verified in several MCT researches [19,23,26].

FTIR spectra analysis was also conducted to identify transformations of structures under milling. The FTIR spectra of original

Fig. 5. Mulliken atomic charge distribution of (a) PeCB-O•, (b) 2,3,4,5-TeCB-O•, (c) 3,4,5-TrCB-O• and (d) 3,4-DCB-O• (The red color refers to the most negative charge while green for positive). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Al₂O₃, milled Al₂O₃, original HCB and milled HCB + Al₂O₃ samples are shown in Fig. 3. The evident differences between the spectra of original and milled Al₂O₃ might be due to the water transformations on the surface of Al₂O₃. Conforming to the ESR spectra, this result implies that MCT destruct the original water species and hydroxyl groups on the surface of Al₂O₃. Peaks at the position of 696 and 932 cm⁻¹ indicate the C–Cl stretching vibration of HCB molecules [63]. Peaks at 1296, 1343, and 1443 cm⁻¹ can be conventionally attributed to benzene rings. In the spectrum of milled HCB + Al₂O₃ samples, peaks of the C–Cl stretching vibration were overlapped with the vibration of Al–O bond. The peaks (C–H vibration of aromatic compounds) at the positions around 1072 and 3097 cm⁻¹ were mainly from the dechlorination intermediates of HCB. The new peak exhibited at 1640 cm⁻¹ was resulted from the vibration of C=O bonds and could be used as the monitor of CB-O•. The above findings clearly demonstrated the dechlorination of HCB and the formation of CB-O•.

XPS was applied to detect the chemical environment of oxygen (Fig. 4). For the original Al₂O₃, two typical peaks were measured at 531.45 eV and 532.20 eV, which are attributed to the oxygen with different reactivity in Al₂O₃. The former indicates the inert oxygen in the lattice, while the relative active oxygen on the surface for the latter. The milling process would increase the surface area and promote the deprotonation reaction (as mentioned in the ESR and FTIR analysis), so the former peak became weaker and the latter one was stronger along with the milling. In other words, the inert

lattice oxygen transforms into the active oxygen on surfaces, which could dramatically increase the reactivity of the MCT. Moreover, a new peak indicating the phenoxyl radical (530.8 eV) appeared after 30 min milling, demonstrating the formation of CB-O• in the MCT process.

3.3. Dechlorination pathways of HCB and formation of peCB-O• predicted by quantum chemical calculation

The abundance of PeCB in the milling process showed in Fig. 1 indicated the speedy dechlorination of HCB, which should be mainly from the reactions of HCB with the electrons and active O²⁻ on Al₂O₃ surface. This process might be the preferred dechlorination pathway in the mechanochemical system and was modeled by quantum chemical calculation in this study. The values of ΔG for the major reactions among HCB, O²⁻ and electrons were calculated and shown in equations (1–4).

Hexachlorobenzene anion (HCB⁻) could be produced when the HCB molecule encounters the electron-rich activated surface

Fig. 6. Total electron density mapped with electrostatic potential surface of (a) PeCB-O•, (b) 2,3,4,5-TeCB-O•, (c) 3,4,5-TrCB-O• and (d) 3,4-DCB-O• (The red color refers to the positive ESP values while blue for negative ones. The numerical values present the internal charge separation in kcal/mol. Orange points are the maximal values and green points are the minimums. Some of them are at the backside.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

induced by grinding, as shown in equation (1) [26,33,64,65]. This reaction is an endothermic process, so certain amounts of energy was needed to promote the reaction. Then, the redundant electron in the HCB molecule causes the relatively strong electronegativity and weakens C–Cl bond of HCB⁻¹. The mean C–Cl bond length of HCB⁻¹ is about 0.02 Å higher than that of HCB, leading to a tendency to dissociate. The HCB⁻¹ would yield a PeCB radical (PeCB•) and a stable ionic chlorine (Cl⁻), as shown in equation (2), which is an exothermic reaction. Calculation results also validated this rule; energy released for dissociating into PeCB• and Cl⁻ was much higher than that for PeCB⁻ and Cl•, as shown in equation (3). Finally, equation (4) shows the generation of the pentachlorinated phenoxyl radical (PeCB-O•), which occurs between PeCB• and active oxygen (O²⁻). In these reactions, oxides act as electron and oxygen donors, inducing formation of HCB⁻¹ and PeCB-O• [23].

3.4. Dechlorination routes from PeCB to MCB predicted by quantum chemical descriptors

According to the above analysis, the CB-O• based pathways were supposed to be the major routes of dechlorination of HCB. The fate of the radicals after removal of one chlorine might have two possibilities at least: 1) reaction with inorganic species (e.g. O²⁻ or occasionally water) leads to further dehalogenation, and the products are hydrogenated by the solvent; 2) reaction with other organic intermediates (e.g. CB-O• or CB•) after chlorine expulsion. The lat-

ter can bring to polymerization and carbonization, which is a very well-known process under milling [21,25]. The present study aims to elucidate the mechanochemical mechanism of rapid dechlorination and research on the chief radicals in this system, so the polymerization pathway was not described in detail. Actually, in the milling jar, possible sources of hydrogen are confined to atmospheric humidity and water in the oxides (adsorbed water, crystal water and bound water), besides, the amounts are also limited. To simplify the quantum chemical calculations and catch the nature of dechlorination in the MCT, the hydrogen addition was supposed to currently happen just after the loss of chlorine. Main dechlorination products of all of the oxygen containing low-chlorinated radicals, including PeCB-O•, TeCB-O•, TrCB-O•, and DCB-O•, were predicted by four quantum chemical descriptors. Atomic charge and ESP analysis pay attention to the electrostatic effects at different sites, while FMO and dual descriptor mainly focus on the difference of electron density [44]. The electrostatic effects determine whether the radical can be pulled into the reaction site to attack the C–Cl bond, and the difficulty level of the bond breakage depends on the electron density at the site. Therefore, both of electrostatic effects and electron density should be considered to gain a more accurate identification of reaction route.

Atomic charge, one of the most simplest and straightforward chemical descriptors in chemical systems, was employed to predict the active sites and the dechlorination route [66]. In general, substitution was preferred to take place at the position of the car-

Fig. 7. Isodensity surfaces of LUMO and LUMO + HOMO orbitals of (a) (b) PeCB-O•, (c) (d) 2,3,4,5-TeCB-O•, (e) (f) 3,4,5-TrCB-O• and (g) (h) 3,4-DCB-O• with an isovalue of 0.09 (Computed $2FED^2_{LUMO}$ and $FED^2_{HOMO} + FED^2_{LUMO}$ are depicted in corresponding sites. The red and blue color refer to different orbital phases of LUMO orbitals. The silver color and black colors refer to different orbital phases of HOMO orbitals. Blue arrows imply positions from which the chlorine atoms tend to be eliminated.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

bon with the highest negative charge density (the lowest atomic charge), which has been viewed as the rule of thumb of reductive dechlorination pathways [67]. All of the atomic charges of carbon atoms in the dominant low-chlorinated radicals were calculated by

methods of Mulliken population [68], Hirshfeld population [42,69] and MK ESP fitting charge [70].

Table 1 displays atomic charges of the major CB-O• formed during the stepwise dechlorination. For PeCB-O•, atom 2(C) and

Fig. 8. Dual descriptor isodensity surfaces and condensed dual descriptors of each atom calculated by Mulliken population of (a) PeCB-O• with an isovalue of 0.03, (b) 2,3,4,5-TeCB-O• with an isovalue of 0.06, (c) 3,4,5-TrCB-O• with an isovalue of 0.007 and (d) 3,4-DCB-O• with an isovalue of 0.01 (The blue color means the negative isosurfaces and the green for positive regions. Blue arrows imply positions from which the chlorine atoms tend to be eliminated.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

6(C) possessed the lowest charges among the five substituent sites, thus the Cl on the sites of 2 and 6 are the most active in the radical, indicating that 2,3,4,5-TeCB-O• is the major tetrachlorinated product. Similarly, Cl atoms at the sites of 6, 3/4 and 4 are the relative active sites for 2,3,4,5-TrCB-O•, 3,4,5-TrCB-O• and 3,4-DCB-O•, resulting in the main intermediates of 3,4,5-TrCB-O•, 3,4-DCB-O• and 3-MCB-O• for the trichlorinated, dichlorinated and monochlorinated isomers. Finally, the last chlorine would be removed and achieved the complete dechlorination. When samples were dissolved into hexane during the extraction procedure, C–O bonds of CB-O• would split and form corresponding chlorobenzenes by hydrogenation, which can be described as hydrodeoxygenation. Based on the naming rules of CB-O• and chlorobenzene, serial numbers would change and the main contents should be 1,2,3,4-TeCB, 1,2,3-TrCB, 1,2-DCB and MCB. Therefore, the main dechlorination route predicted by atomic charge can be depicted as HCB → PeCB → 1,2,3,4-TeCB → 1,2,3-TrCB → 1,2-DCB → MCB, agreed well with the experimental results shown in Fig. 1.

Moreover, Fig. 5(a–d) depicts changes of atomic charge during the dechlorination from PeCB to MCB by Mulliken analysis. The red color refers to the most negative charge while the green color for the most positive one. It can be seen that only the carbon atom linked to oxygen possessed positive charge, and carbon atoms substituted by chlorine hold more positive charges than other atoms linked to hydrogen. This might be because the electron attracting ability follows the order: oxygen > chlorine > hydrogen, and the strong electron attracting ability result in the positive charges of their linked atoms. As a consequence of the strong electron attracting ability, after eliminating one chlorine, the oxygen charge of

2,3,4,5-TeCB-O• was about 0.15 lower than that of PeCB-O•, shown in Fig. 5(a,b), while other atoms varied little. Therefore, the addition of oxygen into radicals would affect the charge distribution and then result in different regioselectivity compared to radicals without oxygen.

Electrostatic potential (ESP) is a significant feature to study the regioselectivity of dechlorination. The atom with more positive ESP is more susceptible to be a reactive site of reductive dechlorination. However, hydrogen atoms would lead to the maximum points deviate from the right locations, resulting in inappropriate determination of the reactive sites [44]. The internal charge separation (Pi) can be used as a substitution to illustrate the reaction route. Pi, a parameter calculated in the ESP calculation process, is viewed as an indicator of charge separation. Negative charges around the oxygen atom lead to the relative deep ESP wells in the neighborhood, which might be active sites for dechlorination reaction. ESP distribution of the major CB-O• formed during the stepwise dechlorination is shown in Fig. 6(a–d). It could be found in Fig. 6(a) that the ortho-positions of PeCB-O•, ortho-position of 2,3,4,5-TeCB-O•, meta-positions of 3,4,5-TrCB-O• and meta-position of 3,4-DCB-O• hold the maximum Pi values of corresponding radicals. Therefore, the dominant low-chlorinated isomers should be PeCB, 1,2,3,4-TeCB, 1,2,3-TrCB and 1,2-DCB, fitting well with the results measured by GC–MS.

FMO theory describes chemical reactivity to interactions between the highest occupied molecular orbital (HOMO) of one species and the lowest unoccupied molecular orbital (LUMO) of the other. The direct reductive dechlorination usually occurs at the atoms with higher $2FED_{LUMO}^2$, while the radical attack can more probably take place at sites with higher values of

that 1,2,3,4-TeCB, 1,2,3-TrCB and 1,2-DCB were the main intermediates. Whereas, as shown in Fig. 7(g, h), 2FED²_{LUMO} revealed that meta-position is the most active sites for 3,4-DCB-O[•], while FED²_{HOMO} + FED²_{LUMO} implied the para-position. Compared with the atomic charge analysis, FED²_{HOMO} + FED²_{LUMO} is more appropri-

Table 2

Atomic charge of PeCB, 1,2,3,5-TeCB, 1,2,4,5-TeCB, 1,2,4-TrCB, 1,3,5-TrCB and 1,3-DCB calculated by Mulliken population, Hirshfeld population and MK ESP fitting charge analysis.

Structure	Atom	Mulliken	Hirshfeld	MK ESP
	1	-0.1215	-0.0441	-0.0555
	2	-0.0660	0.0235	-0.0016
	3	-0.0791	0.0126	0.0773
	4	-0.0791	0.0174	0.0119
	5	-0.0791	0.0126	0.0773
	6	-0.0660	0.0235	-0.0038
	1	-0.1224	-0.0462	-0.0345
	2	-0.0602	0.0324	-0.0195
	3	-0.1224	-0.0047	-0.0345
	4	-0.0702	0.0267	-0.0161
	5	-0.0823	0.0105	0.1193
	6	-0.0702	0.0267	-0.0161
	1	-0.0125	-0.0411	-0.0942
	2	-0.0696	0.0219	0.0463
	3	-0.0696	0.0219	0.0463
	4	-0.0125	-0.0411	-0.0942
	5	-0.0696	0.0219	0.0449
	6	-0.0696	0.0219	0.0449
	1	-0.1246	-0.0334	-0.1314
	2	-0.1217	-0.0383	-0.0845
	3	-0.0626	0.0294	0.0129
	4	-0.1255	-0.0448	-0.0545
	5	-0.0719	0.0237	0.0383
	6	-0.0732	0.0182	0.0703
	1	-0.1240	-0.0492	-0.0182
	2	-0.0646	0.0354	-0.0199
	3	-0.1240	-0.0492	-0.0160
	4	-0.0646	0.0354	-0.0214
	5	-0.1240	-0.0492	-0.0160
	6	-0.0646	0.0354	-0.0199
	1	-0.1260	-0.0272	-0.1751
	2	-0.1249	-0.0440	-0.0603
	3	-0.0645	0.0307	0.0139
	4	-0.1249	-0.0492	-0.0226
	5	-0.0645	0.0307	0.0127
	6	-0.1249	-0.0440	-0.0603

Fig. 10. Comparison of the primary $\text{CB-O}^\bullet$ based pathway and the main pathways with $\text{CB}^\bullet$.

ate for our reaction, and this discrepancy might reveal that radical attack is the dechlorination pathway for our reaction system.

It was generally proposed in the dual descriptor analysis that the position with higher value contributes more to positive regions and LUMO and is much easier for dechlorination [41,72]. The condensed dual descriptors of each atom were calculated by Mulliken population method in this study. As shown in Fig. 8(a-d), dual descriptor analysis exhibited excellent reproducibility of experimental results

on the dechlorination of $\text{PeCB-O}^\bullet$, $2,3,4,5\text{-TeCB-O}^\bullet$, $3,4,5\text{-TrCB-O}^\bullet$ and $3,4\text{-DCB-O}^\bullet$, consistent with the experimental results. In general, all of the four quantum chemical descriptors can precisely reveal the dechlorination route of $\text{CB-O}^\bullet$.

Based on both the experimental results and quantum chemical calculations, the $\text{CB-O}^\bullet$ based stepwise dechlorination mechanism for the MCT of HCB was proposed and shown in Fig. 9. Herein, the dechlorination and hydrogenation was described, however,

dehalogenation is not the only process occurred during milling. The organic radicals might also react with other organic species. This is the pathway lead to polymerization and final carbonization. Degradation of the organic structure is also another process and the main responsible for the generation of amorphous/graphitic carbon [27]. This intriguing problem will be elucidated through the unite method of experiments and quantum chemical calculations in the near future.

3.5. Impacts of different radical reactions on the dechlorination of HCB

Considering the complexity of MCT process and radical reactions, $\text{CB}^\bullet$ based dechlorination might be another pathway of HCB's decomposition. If some of the $\text{PeCB}^\bullet$ have no chance to react with O^{2-} after chlorine expulsion induced by the capture of a trapped electron on the Al_2O_3 or Al surface, then the dechlorination will proceed on with $\text{PeCB}^\bullet$, $\text{TeCB}^\bullet$, $\text{TrCB}^\bullet$ and $\text{DCB}^\bullet$, similar to the photocatalytic degradation mechanism [73]. However, $\text{CB}^\bullet$ based photodegradation of HCB demonstrates that meta-Cl and para-Cl are the easiest sites to be removed [73]. This conspicuous discrepancy implies a vast difference in the active sites for dechlorination between $\text{CB-O}^\bullet$ and $\text{CB}^\bullet$, showing that $\text{CB}^\bullet$ based process is only a minor pathway for HCB's decomposition in the MCT.

Mulliken population, Hirshfeld population and MK ESP fitting charge of PeCB , 1,2,3,5- TeCB , 1,2,4,5- TeCB , 1,2,4- TrCB , 1,3,5- TrCB and 1,3- DCB were also calculated to theoretically elucidate the $\text{CB}^\bullet$ based dechlorination routes (given in Table 2). Except MK ESP fitting charge, atomic charges of the meta-positions (atom 3(C) and 5 (C)) were the lowest and the para-C (atom 4(C)) hold the same Mulliken charge with the meta-positions. This analysis is consistent with the main experimental route that 1,2,4,5- TeCB and 1,2,3,5- TeCB were the main TeCB s. For 1,2,3,5- TeCB , atom 5(C) possessed the lowest charge among the four substituent sites, thus 1,3,5- TrCB might be its primary TrCB product. 1,2,4- TeCB is the single TrCB product of 1,2,4,5- TeCB due to the symmetry and 1,3- DCB is the main product for 1,2,4- TeCB . In addition, 1,2,3,5- TeCB is preferred to produce 1,3,5- TrCB with 1,3- DCB as the sole DCB product. The main $\text{CB}^\bullet$ based dechlorination routes were predicted as $\text{HCB} \rightarrow \text{PeCB} \rightarrow 1,2,3,5\text{-TeCB}/1,2,4,5\text{-TeCB} \rightarrow 1,3,5\text{-TrCB}/1,2,4\text{-TrCB} \rightarrow 1,3\text{-DCB} \rightarrow \text{MCB}$, as depicted in Fig. 10, dissimilar to the primary $\text{CB-O}^\bullet$ based pathway. Both of the dominant intermediates and quantum chemical descriptor analysis confirms that dechlorination pathway based on $\text{CB-O}^\bullet$ prevails in the MCT process.

4. Conclusions

In this paper, the mechanochemical mechanism of rapid dechlorination of HCB was studied by both experiments and quantum chemical calculations. The step-wise dechlorination pathways of HCB in the MCT process was proposed and testified by quantum chemical descriptor analysis. The main results can be concluded as follows:

- (1) HCB can be degraded in the MCT process with Al and Al_2O_3 as co-milling reagents in about 60 min. Characterization of ESR, FTIR and XPS testified that the dechlorination route of HCB mainly proceed via the routes deduced by $\text{CB-O}^\bullet$ radicals.
- (2) Thermodynamic calculations and quantum chemical descriptors successfully predicted the dechlorination pathways of HCB in the MCT process.
- (3) Comparisons of the mechanochemical and photochemical dechlorination of HCB showed that the intermediate products are different in these two processes. The former is based on $\text{CB-O}^\bullet$, while the latter is based on $\text{CB}^\bullet$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2017.03.022>.

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