Science of the Total Environment 408 (2010) 2549–2554

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Dechlorination pathways of diverse chlorinated aromatic pollutants conducted by *Dehalococcoides* sp. strain CBDB1

Gui-Ning Lu [a,c,d], Xue-Qin Tao [b], Weilin Huang [c], Zhi Dang [a,e,*], Zhong Li [d], Cong-Qiang Liu [f]

[a] School of Environmental Science and Engineering, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, PR China
[b] School of Environmental Science and Engineering, Zhongkai University of Agriculture and Engineering, Guangzhou 510225, PR China
[c] Department of Environmental Sciences, Rutgers, The State University of New Jersey, New Brunswick, NJ 08901, United States
[d] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China
[e] The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, PR China
[f] The State Key Lab of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, PR China

ARTICLE INFO

Article history:
Received 9 August 2009
Received in revised form 9 February 2010
Accepted 2 March 2010
Available online 26 March 2010

Keywords:
Chlorinated aromatic pollutant
Dehalococcoides sp. strain CBDB1
Mulliken atomic charges
Reductive dechlorination
Theoretical indicator

ABSTRACT

Dechlorination of chlorinated aromatic pollutants (CAPs) has become a major issue in recent decades. This paper reported a theoretical indicator for predicting the reductive dechlorination pathways of polychlorinated dibenzo-*p*-dioxins (PCDDs), chlorobenzenes and chlorophenols transformed by *Dehalococcoides* sp. strain CBDB1. Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d) level for all related CAPs and Mulliken atomic charges on chlorine atoms ($Q_{Cl(n)}$) were adopted as the probe of the dechlorination reaction activity. $Q_{Cl(n)}$ can consistently indicate the main dechlorination daughter products of PCDDs, chlorobenzenes and chlorophenols conducted by strain CBDB1. The dechlorination reaction favors elimination of the chlorine atoms having greater $Q_{Cl(n)}$ values. The chlorine atom with the greatest $Q_{Cl(n)}$ value tends preferentially to be eliminated, whereas the chlorine atom with the smallest $Q_{Cl(n)}$ value tends unlikely to be eliminated or does not react at all. For a series of compounds having similar structure, the maximal $Q_{Cl(n)}$ of each molecular can be used to predict the possibility of its daughter product(s). In addition, the difference ($\Delta Q_{Cl(n)}$) between the maximal $Q_{Cl(n)}$ and the next maximal $Q_{Cl(n)}$ of the same molecule can be used to assess the possibility of formation of multiple dechlorination products.

1. Introduction

Chlorinated aromatic pollutants (CAPs) such as polychlorinated biphenyls (PCBs) and chlorinated benzenes are widespread persistent contaminants in soils and sediments (Fennell et al., 2004). It is of particular importance to develop effective technologies for remedy of CAP-contaminated soils and sediments. Several transformation-based technologies including photolysis, photocatalysis, γ-radiolysis, biodegradation, incineration and thermal treatment have been developed for destruction of these chemicals in different environmental systems (Adriaens et al., 1996; Choi et al., 2000; Kluyev et al., 2002; Konstantinov et al., 2000; Fennell et al., 2004; Mitoma et al., 2004; Lundin and Marklund, 2005; Noma et al., 2007; Wang et al., 2008). The use of microorganisms for in situ remediation is regarded as a better and inexpensive method to detoxify CAPs from the environment (Fennell et al., 2004).

Reductive dechlorination is an important transformation process for CAPs in the environment (Fennell et al., 2004). *Dehalococcoides* strains are highly specialized and strictly anaerobic bacteria that are known to grow only by respiration using hydrogen as an electron donor and halogenated organic compounds as electron acceptors (Adrian et al., 2007). Neither fermentation nor respiration with non-halogenated compounds has been observed with any of the described isolates (Bunge et al., 2003; Holscher et al., 2003; Fennell et al., 2004; Adrian et al., 2007; Liu and Fennell, 2008). *Dehalococcoides* sp. strain CBDB1 was found to dechlorinate 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD), 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (1,2,3,7,8-PeCDD), hexachlorobenzene (HxCB), pentachlorophenol (PeCP) and some of their daughter products (Bunge et al., 2003; Holscher et al., 2003; Adrian et al., 2007). Despite the above studies having provided insight information on the dechlorination of selected CAPs, the dechlorination reaction pathways by strain CBDB1 for most CAPs have not yet been clearly delineated in the literature.

Practically speaking, experimental determination of dechlorination pathways is technically difficult for some CAPs such as polychlorinated dibenzo-*p*-dioxins (PCDDs) that undergo degradation at extremely slow rates. Some intermediate products of CAP degradation may not be detected since they are not commercially available. Thus, it is necessary to develop theoretical approaches to predict the dechlorination pathways and products. One of these techniques is based on structure–activity relations (SARs) that correlates certain molecular descriptors

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* Corresponding author. School of Environmental Science and Engineering, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, PR China. Tel.: +86 20 39380522; fax: +86 20 39380569.
E-mail address: chzdang@scut.edu.cn (Z. Dang).

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doi:10.1016/j.scitotenv.2010.03.003

calculated directly from chemical structures to the dechlorination activity of different CAPs.

In this work, we employed density functional theory (DFT) calculations (Becke, 1993; Putz, 2008a) to gather structural information of CAPs. We identified the structural descriptors that may be best indicators for experimentally determined dechlorination pathways for limited sets of CAPs in the presence of *Dehalococcoides* sp. strain CBDB1. After validation of the probe for the dechlorination reaction activity, we could propose the most likely pathways for the dechlorination of a large set of CAPs.

2. Experimental section

The molecular modeling system HyperChem (Release 7.0, Hypercube Inc., 2002) was used to construct and view the structures of all CAPs examined in this study. Molecular geometry was optimized using the B3LYP hybrid functional of DFT in conjunction with 6-31G(d), a split-valence basis set with polarization function (Hehre et al., 1972; Becke, 1993). DFT was selected because it has been widely used in recent applications of quantum chemistry (Zhou et al., 2005; Zhang et al., 2006; Lu et al., 2008; Tao et al., 2008). In addition, the computational time of DFT calculations is now much shorter than before since the computing speed of the personal computer has increased dramatically. B3LYP/6-31G(d) was selected because it was reliable in computing structure descriptors of aromatic organic compounds (Yang et al., 2006). The stability of molecular structures was confirmed by the vibrational frequency analysis. All calculations were carried out with the Gaussian 03 program (Frisch et al., 2003) running on an Intel Core 2 Duo 3.00 GHz CPU computer equipped with 5.00 GB of internal memory and Microsoft Windows XP Professional operating system.

DFT calculations were performed for all related CAPs, resulting in useful structural descriptors of these compounds. These descriptors include the eigenvalue of the highest occupied/lowest unoccupied molecular orbital ($E_{\mathrm{HOMO}}/E_{\mathrm{LUMO}}$), the molecular total energy (E_{T}), the electronic spatial extent (R_e), the dipole moment (μ), the Mulliken atomic charge on carbon and chlorine atoms ($Q_{\mathrm{C}(n)}$ and $Q_{\mathrm{Cl}(n)}$, n is the carbon atom number in the frame), the bond length between carbon and its substituted chlorine atoms (L_n). These descriptors were correlated with the experimentally determined dechlorination pathways of CAPs in the presence of *Dehalococcoides* sp. strain CBDB1 (Bunge et al., 2003; Holscher et al., 2003; Adrian et al., 2007). The descriptors that were validated as the indicators for the reported dechlorination pathways of limited sets of CAPs were thus used to propose the dechlorination pathways for other CAPs.

3. Results

After validation of experimental dechlorination pathways of CAPs by *Dehalococcoides* sp. strain CBDB1 (Bunge et al., 2003; Holscher et al., 2003; Adrian et al., 2007), the Mulliken atomic charge on chlorine atoms ($Q_{\mathrm{Cl}(n)}$) is adopted as the theoretical indicator of the dechlorination reaction activity. According to our calculation, the dechlorination reaction favors elimination of the chlorine atoms having greater $Q_{\mathrm{Cl}(n)}$ values. In other words, on the same CAP molecule, the chlorine atom with the greatest $Q_{\mathrm{Cl}(n)}$ value tends to be eliminated preferentially by the microorganisms, whereas the chlorine atom with the smallest $Q_{\mathrm{Cl}(n)}$ value tends to be least likely eliminated or may not be reactive at all.

3.1. Validation of the dechlorination pathways of PCDDs

Bunge et al. (2003) reported that *Dehalococcoides* sp. strain CBDB1 could dechlorinate 1,2,3,4-TCDD and 1,2,3,7,8-PeCDD to a series of less chlorinated PCDDs, respectively. The dechlorination pathways are shown in Fig. 1.

We examined the structural parameters computed from DFT and found a good positive correlation between the $Q_{\mathrm{Cl}(n)}$ of PCDDs and their reactivity. Table 1 lists the $Q_{\mathrm{Cl}(n)}$ values of the related PCDDs examined in Bunge et al. (2003). As can be seen in Table 1, for 1,2,3,4-TCDD, the Mulliken atomic charges on the positions 1 and 4 are 0.06413 and on the positions 2 and 3 are 0.05899. According to Fig. 1, the dechlorination reactions at the positions 1 and 4 are preferred over those at the positions 2 and 3, resulting in accumulation of 1,2,3-TrCDD as the intermediate product. The three chlorines on 1,2,3-TrCDD have Mulliken atomic charges on the order of $Q_{\mathrm{Cl}(1)}$ (0.05812)$>Q_{\mathrm{Cl}(2)}$ (0.05222)$>Q_{\mathrm{Cl}(3)}$ (0.02634), and the detected experimental dechlorination main product 2,3-DCDD is resulted from the dechlorination of position 1.

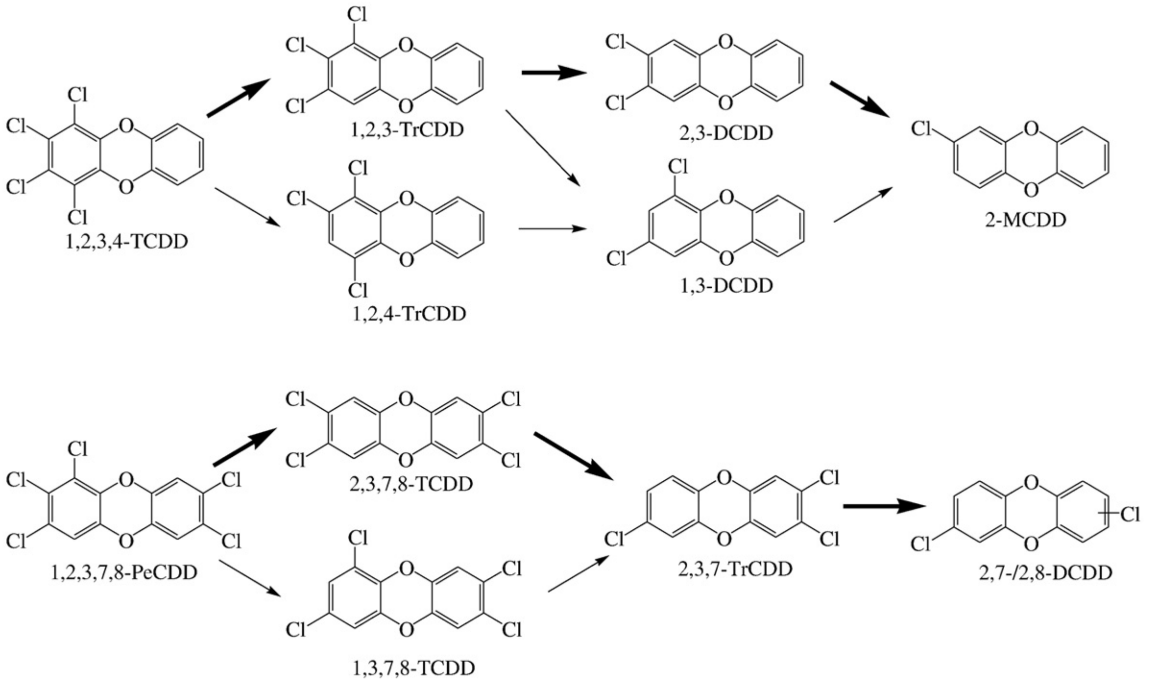

Fig. 1. Dechlorination pathways of two PCDDs by *Dehalococcoides* sp. strain CBDB1 (Bunge et al., 2003). The major routes are marked with bold arrows.

Table 1
Mulliken atomic charges of chlorine atoms for selected PCDDs.

PCDDs	$Q_{\mathrm{Cl}(n)}$[a]					
	1	2	3	4/7	8	Δ[b]
1,2,3,7,8-PeCDD	**0.06606**	0.05914	0.03402	0.02995	0.02912	0.00692
2,3,7,8-TCDD	–	**0.02650**	**0.02650**	**0.02650**	**0.02650**	–
1,3,7,8-TCDD	**0.03256**	–	0.00214	0.02762	0.02678	0.00494
2,3,7-TrCDD	–	0.02306	**0.02327**	−0.01068	–	0.00021
1,2,3,4-TCDD	**0.06413**	0.05899	0.05899	**0.06413**	–	0.00514
1,2,3-TrCDD	**0.05812**	0.05222	0.02634	–	–	0.00590
1,2,4-TrCDD	**0.05659**	0.02627	–	0.03011	–	0.02648
2,3-DCDD	–	**0.01868**	**0.01868**	–	–	–
1,3-DCDD	**0.02365**	–	−0.00621	–	–	0.02986

[a] Given in bold are the maximal $Q_{\mathrm{Cl}(n)}$.
[b] Δ is the gap between the maximal and the next maximal $Q_{\mathrm{Cl}(n)}$.

Table 2
Dechlorination products of selected chlorobenzenes in crude extracts of *Dehalococcoides* sp. strain CBDB1 (Holscher et al., 2003).

Added chlorobenzenes	Dechlorination products	Specific activity ± SD[a] (nkat/mg of protein)[b]
1,2,3-TrCB	1,3-DCB	11 ± 0.7
1,2,4-TrCB	1,3-/1,4-DCB	0.3 ± 0.0
1,3,5-TrCB	–	<0.05
1,2,3,4-TCB	1,2,4-TrCB	355 ± 21
1,2,3,5-TCB	1,3,5-TrCB	76 ± 1.7
1,2,4,5-TCB	1,2,4-TrCB	3 ± 0.1
PeCB	1,2,3,5-/1,2,4,5-TCB	171 ± 12
HxCB	PeCB	0.4 ± 0.0

[a] Means of results of triplicate assays ± standard deviation.
[b] 1 nkat is defined as 1 nmol of dechlorination products formed per second at 25 °C.

For all PCDDs listed in Table 1, the main products of dechlorination proposed by the maximal $Q_{\mathrm{Cl}(n)}$ are exactly the same as the experimentally detected main products shown in Fig. 1. Meanwhile, 1,3,7,8-TCDD, 1,2,4-TrCDD and 1,3-DCDD were identified experimentally as the secondary products of 1,2,3,7,8-PeCDD, 1,2,3,4-TCDD and 1,2,3-TrCDD, respectively. These secondary products are formed by dechlorination at the positions having the next maximal $Q_{\mathrm{Cl}(n)}$. Therefore, it could be concluded that the dechlorination reaction of PCDDs by *Dehalococcoides* sp. strain CBDB1 favors elimination of the chlorine atoms having greater $Q_{\mathrm{Cl}(n)}$ values. In other words, the chlorine atom having maximal $Q_{\mathrm{Cl}(n)}$ value tends to be preferentially eliminated.

Further study of the data listed in Table 1 indicates that the three PCDDs having two detected experimental products satisfy two conditions: (1) the difference ($\Delta Q_{\mathrm{Cl}(n)}$) between the maximal $Q_{\mathrm{Cl}(n)}$ and the next maximal $Q_{\mathrm{Cl}(n)}$ of the three parent PCDDs is <0.01 and (2) the next maximal $Q_{\mathrm{Cl}(n)}$ is >0.05. In the case of 1,3,7,8-TCDD, the $\Delta Q_{\mathrm{Cl}(n)}$ is <0.01, but its next maximal $Q_{\mathrm{Cl}(n)}$ is <0.03. It indicates weaker reactivity of the second chlorine atom, hence only one dechlorination product was detected experimentally for 1,3,7,8-TCDD. Since 2,7-DCDD and 2,8-DCDD were not separated under experimental conditions, both were considered as the dechlorination product of 2,3,7-TrCDD (Bunge et al., 2003). As shown in Table 1, the $\Delta Q_{\mathrm{Cl}(n)}$ of 2,3,7-TrCDD is <0.01 and its next maximal $Q_{\mathrm{Cl}(n)}$ is <0.03, so we predict that 2,7-DCDD may be the only dechlorination product. For the other four PCDDs listed in Table 1, they either have $\Delta Q_{\mathrm{Cl}(n)} > 0.01$ or structurally have only one dechlorination product. Therefore, only one dechlorination product was detected experimentally for each. According to the above analysis, it can be concluded that $\Delta Q_{\mathrm{Cl}(n)}$ can be used as an indicator for assessing whether a secondary dechlorination product of PCDDs by *Dehalococcoides* sp. strain CBDB1 may be present. The smaller $\Delta Q_{\mathrm{Cl}(n)}$ value may indicate high possibility of formation of a secondary dechlorination product.

3.2. Validation of the dechlorination pathways of chlorobenzenes

Holscher et al. (2003) reported the reductive dehalogenation of chlorobenzenes (CBs) in cell extracts of *Dehalococcoides* sp. strain CBDB1. The reported dechlorination products and dehalogenase activity in crude extracts are listed in Table 2. The calculated $Q_{\mathrm{Cl}(n)}$ values of the related CBs are listed in Table 3.

The proposed dechlorination pathways of CBs based on the maximal $Q_{\mathrm{Cl}(n)}$ are shown in Fig. 2 (see solid arrows). Comparing Fig. 2 with Table 2, we found all the proposed dechlorination products pointed by solid arrows had been detected experimentally. Both pentachlorobenzene (PeCB) and 1,2,4-trichlorobenzene (1,2,4-TrCB) had two experimental dechlorination products (Holscher et al., 2003). As the second dechlorination products, 1,2,3,5-tetrachlorobenzene (1,2,3,5-TCB) and 1,3-dichlorobenzene (1,3-DCB) are resulted from the dechlorination of PeCB and 1,2,4-TrCB on the positions having the next maximal $Q_{\mathrm{Cl}(n)}$, respectively. Both the $\Delta Q_{\mathrm{Cl}(n)}$ of PeCB and 1,2,4-TrCB are <0.01 (see Table 3), indicating a possibility of formation of two dechlorination products. For other CBs listed in Table 3, the $\Delta Q_{\mathrm{Cl}(n)}$ values are >0.01 or the chemicals are limited structurally to only one dechlorination product.

Fig. 3 presented the biodegradation rate against the maximal $Q_{\mathrm{Cl}(n)}$ of CBs. It shows that, excluding the data point for HxCB, the measured biodegradation rate of CBs correlates positively with the computed maximal $Q_{\mathrm{Cl}(n)}$ values of the compounds. For example, 1,2,3,4-TCB and PeCB having higher maximal $Q_{\mathrm{Cl}(n)}$ values (0.06250 and 0.07073, respectively) exhibit much faster reaction rates among the listed CBs whereas 1,3,5-TrCB having lower maximal $Q_{\mathrm{Cl}(n)}$ value (0.00539) exhibits slower reaction rate without dechlorination product identified in the reported study. However, HxCB has the largest maximal $Q_{\mathrm{Cl}(n)}$ 0.07587 among the CBs listed in Table 3, but its reaction rate is much slower. The reported degradation rate of HxCB is about 0.4 nkat/mg of protein, which is comparable to the rate for 1,2,4-TrCB (0.3 nkat/mg of protein), but is dramatically lower than 171 nkat/mg of protein for PeCB. It appears that HxCB may be an outliner in this dataset. One possible explanation is that the enzymes of the microorganisms also decide the rate of dechlorination while the theoretical approach only considers the property of the compound.

3.3. Validation of the dechlorination pathways of chlorophenols

Adrian et al. (2007) investigated the growth of *Dehalococcoides* sp. strain CBDB1 with chlorophenols (CPs) as the electron acceptors. They summarized the proposed dechlorination pathways of CP degradation (Fig. 4). Here we calculated the $Q_{\mathrm{Cl}(n)}$ values for the deprotonated CPs because they are readily deprotonated to chlorophenol anions and hydrogen cations in aqueous solution. The calculated $Q_{\mathrm{Cl}(n)}$ values are listed in Table 4.

As shown in Fig. 4 and Table 4, the proposed dechlorination pathways of chlorophenol anions based on the maximal $Q_{\mathrm{Cl}(n)}$ are in accordance with the detected pathways. For example, the dominant dechlorination product of 2,3,5,6-TCP is 2,3,5-TrCP which is further degraded to 3,5-DCP whereas the dominant dechlorination product of 2,3,6-TrCP is 2,5-DCP, and further to 3-MCP. By comparing the maximal $Q_{\mathrm{Cl}(n)}$ value of each chlorophenol anion and the arrow type of the dechlorination pathways shown in Fig. 4, it can be seen that when the maximal $Q_{\mathrm{Cl}(n)}$ value is <-0.14, the dechlorination reaction tends be slow and incomplete or even does not react at all. For instance, the three MCPs and 3,5-DCP do not react at all whereas 2,4- and 2,6-DCP are dechlorinated at very slow rates. However, when the computed maximal $Q_{\mathrm{Cl}(n)}$ value is >-0.11, the dechlorination reaction is complete and the main dechlorination product is consistent with that proposed with the maximal $Q_{\mathrm{Cl}(n)}$. For example, the dechlorination reactions of the three TCPs and PeCP are complete. In addition, for 2,4,6-TrCP and 3,4-DCP having the maximal $Q_{\mathrm{Cl}(n)}$ between -0.14 and -0.11 (about -0.12), the dechlorination reaction of 2,4,6-TrCP is complete, while dechlorination reaction of 3,4-DCP occurred only if it was formed from a higher chlorinated phenol in the same culture.

Table 3
Mulliken atomic charges of chlorine atoms for selected chlorobenzenes.

Chlorobenzenes	$Q_{Cl(n)}$[a]						
	1	2	3	4	5	6	Δ[b]
HxCB	**0.07587**	**0.07587**	**0.07587**	**0.07587**	**0.07587**	**0.07587**	–
PeCB	0.04396	0.06940	**0.07073**	0.06940	0.04396	–	0.00133
1,2,3,4-TCB	0.03250	**0.06250**	**0.06250**	0.03250	–	–	0.03000
1,2,3,5-TCB	0.03801	**0.06294**	0.03801	–	0.01222	–	0.02493
1,2,4,5-TCB	**0.03673**	**0.03673**	–	**0.03673**	**0.03673**	–	–
1,2,3-TrCB	0.02370	**0.05383**	0.02370	–	–	–	0.03013
1,2,4-TrCB	0.02478	**0.02883**	–	−0.00043	–	–	0.00405
1,3,5-TrCB	**0.00539**	–	**0.00539**	–	**0.00539**	–	–
1,2-DCB	**0.01339**	**0.01339**	–	–	–	–	–
1,3-DCB	**−0.01069**	–	**−0.01069**	–	–	–	–
1,4-DCB	**−0.01428**	–	–	**−0.01428**	–	–	–

[a] Given in bold are the maximal $Q_{Cl(n)}$.
[b] Δ is the gap between the maximal and the next maximal $Q_{Cl(n)}$.

For the chlorophenols having two or more detected dechlorination products, the dechlorination always took place in the positions having larger $Q_{Cl(n)}$ values. Further investigation of Table 4 and Fig. 4 indicates that the requirements for a chlorophenol to yield two dechlorination products are that the $\Delta Q_{Cl(n)}$ value of a chlorophenol anion is <0.01. If its third maximal $Q_{Cl(n)}$ is >-0.0875, the chlorophenol may have a tertiary dechlorination product. For example, PeCP, 2,3,4,5-TCP, 2,4,5-TrCP and 3,4-DCP have two or more dechlorination products. Meanwhile, if a chlorophenol anion has $\Delta Q_{Cl(n)}$ of >0.01 and has at least two $Q_{Cl(n)}>-0.0875$, it may have multiple dechlorination products. For example, 2,3,4,6-TCP and 2,3,4-TrCP have two dechlorination products. However, if a chlorophenol anion has $\Delta Q_{Cl(n)}$ value of >0.01 and its next maximal $Q_{Cl(n)}$ is <-0.0875, the compound may have only one dechlorination product or even hard to dechlorinate. For instance, 2,3,6-TrCP has only one dechlorination product.

4. Discussion

We had reported four rules of thumb for predicting the main reductive dechlorination pathways of PCDDs in the presence of zero-valent zinc based on the maximal $Q_{Cl(n)}$ probe (Lu et al., 2010). Since the dechlorination pathways of PCDDs by *Dehalococcoides* sp. strain CBDB1 were indicated by $Q_{Cl(n)}$, their main pathways and products also could follow those rules of thumb. However, the dechlorination pathways of CAPs may differ under different environmental conditions. Studies have shown different dechlorination mechanisms for 1,2,3,4-TCDD conducted by *Dehalococcoides* sp. strain CBDB1(Bunge et al., 2003) and *Dehalococcoides ethenogenes* strain 195 (Fennell et al., 2004). Thus, in addition to the Mulliken charge of the selected atom, other descriptors such as electron affinity, electronegativity and chemical hardness indices may offer alternative perspectives for predicting the dechlorination pathways of CAPs in different systems (Arulmozhiraja and Morita, 2004; Putz, 2008b,c). In a theoretical study, Arulmozhiraja and Morita (2004) hypothesized that the electron attachment on the neutral gaseous PCDFs may weaken the C–Cl bonds and that the dechlorination may take place on the much-elongated C–Cl bonds of the anionic PCDFs. However, this hypothesis was not validated with experimental data. We had considered the C–Cl bond length (L_n) as an alternative probe. However, this probe did not fit well with the experimental results obtained under aqueous conditions and in the presence of *Dehalococcoides* sp. strain CBDB1.

5. Conclusions

DFT calculations were carried out at the B3LYP/6-31G(d) level for selected PCDDs, chlorobenzenes and chlorophenol anions, and Mulliken

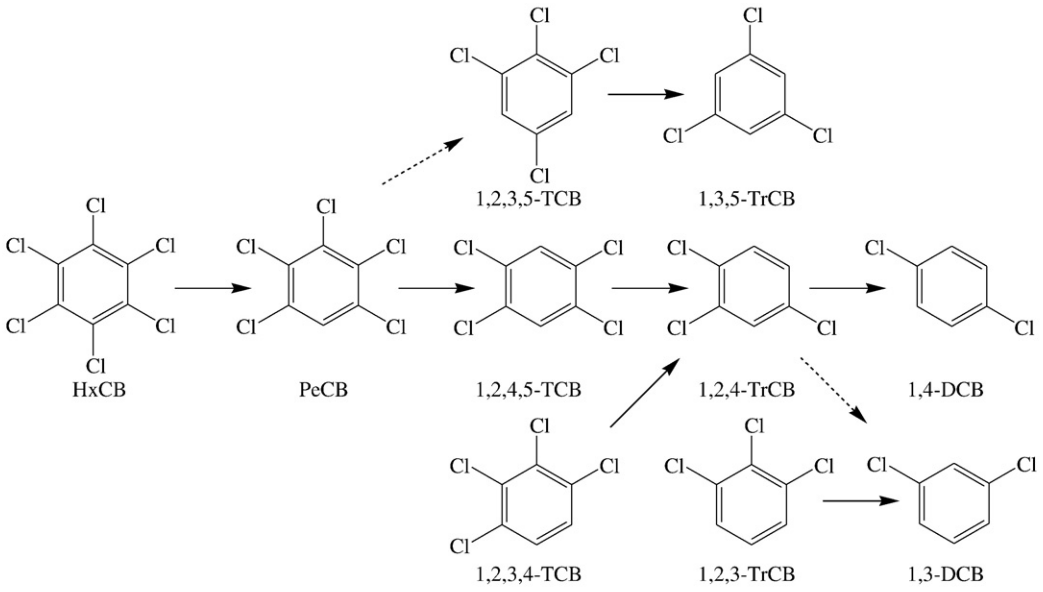

Fig. 2. Dechlorination pathways of chlorobenzenes predicted with the $Q_{Cl(n)}$ probe. The major routes are marked with solid arrows and dashed arrows are predicted by the next maximal $Q_{Cl(n)}$.

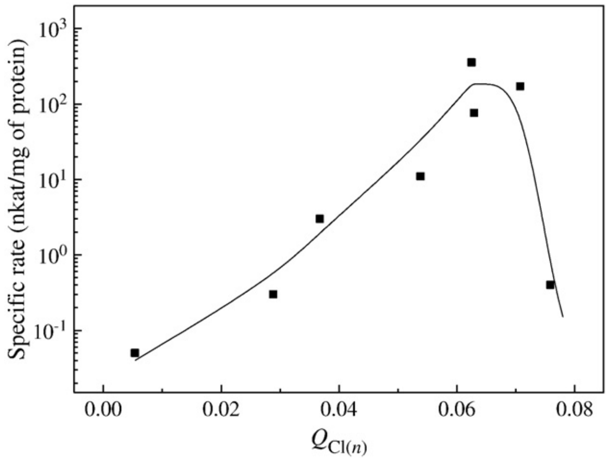

Fig. 3. The experimentally determined reaction rate against the maximal $Q_{Cl(n)}$ of the selected chlorobenzenes.

atomic charges on chlorine atoms ($Q_{Cl(n)}$) were adopted as the probe of the dechlorination reaction activity of *Dehalococcoides* sp. strain CBDB1. $Q_{Cl(n)}$ can consistently indicate the main dechlorination daughter products of PCDDs, chlorobenzenes and chlorophenols by strain CBDB1. The dechlorination reaction favors elimination of the chlorine atoms having greater $Q_{Cl(n)}$ values. The chlorine atom with the greatest $Q_{Cl(n)}$ value tends preferentially to be eliminated, whereas the chlorine atom with the smallest $Q_{Cl(n)}$ value tends unlikely to be eliminated or

Table 4
Mulliken atomic charges of chlorine atoms of chlorophenol anions.

Chlorophenols	$Q_{Cl(n)}$[a]					
	2	3	4	5	6	Δ[b]
PeCP	−0.05840	**−0.03959**	−0.04478	−0.03959	−0.05840	0.00519
2,3,4,5-TCP	−0.07345	**−0.04997**	−0.05522	−0.08814	–	0.00525
2,3,4,6-TCP	−0.06864	**−0.05110**	−0.08780	–	−0.10825	0.01754
2,3,5,6-TCP	**−0.07076**	−0.08448	–	−0.08448	**−0.07076**	0.01372
2,3,4-TrCP	−0.08734	**−0.06444**	−0.10635	–	–	0.02290
2,3,5-TrCP	**−0.08591**	−0.09672	–	−0.13539	–	0.01081
2,3,6-TrCP	**−0.08294**	−0.10325	–	–	−0.12725	0.02031
2,4,5-TrCP	−0.12591	–	**−0.09947**	−0.10158	–	0.00211
2,4,6-TrCP	**−0.11988**	–	−0.13172	–	**−0.11988**	0.01184
3,4,5-TrCP	–	−0.10148	**−0.06589**	−0.10148	–	0.03559
2,3-DCP	**−0.10315**	−0.12021	–	–	–	0.01706
2,4-DCP	**−0.14222**	–	−0.15277	–	–	0.01055
2,5-DCP	**−0.14589**	–	–	−0.15754	–	0.01165
2,6-DCP	**−0.14319**	–	–	–	**−0.14319**	–
3,4-DCP	–	−0.11921	**−0.11888**	–	–	0.00033
3,5-DCP	–	**−0.15051**	–	**−0.15051**	–	–
2-/3-/4-MCP	**−0.16815**	**−0.18004**	**−0.17564**	–	–	–

[a] Computed on chlorophenol anions without the hydrogen atom connected with the oxygen atom and given in bold are the maximal $Q_{Cl(n)}$.
[b] Δ is the gap between the maximal and the next maximal $Q_{Cl(n)}$.

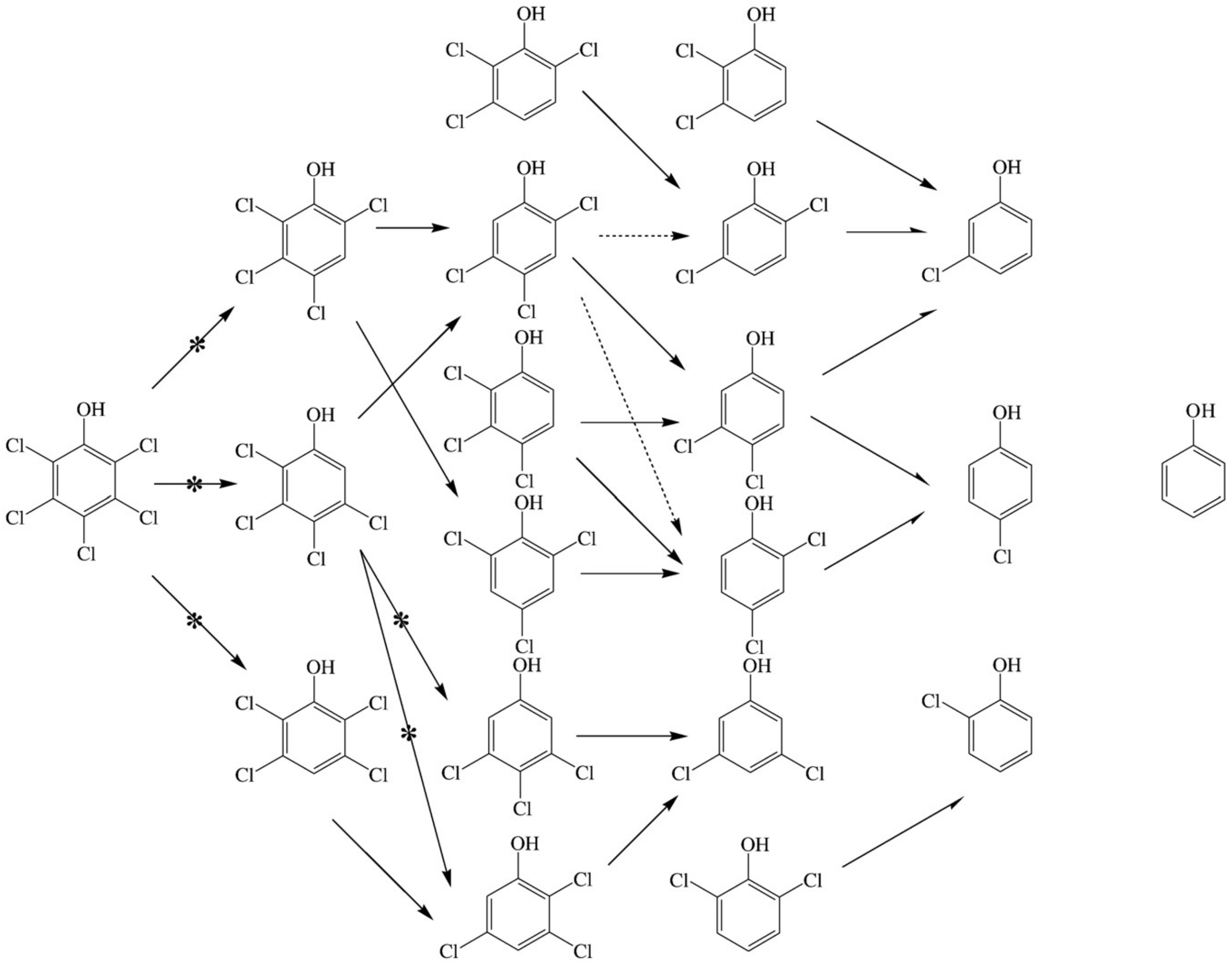

Fig. 4. Dechlorination pathways of chlorophenols by *Dehalococcoides* sp. strain CBDB1 (Adrian et al., 2007). Solid arrows: main pathway; dashed arrows: side pathway; downside arrows: slow and incomplete reactions; upside arrows: reactions that occurred only if the respective chlorophenol was formed from a higher chlorinated phenol in the same culture. The asterisks mark reactions where the pathways could not be distinguished.

does not react at all. In addition, the $\Delta Q_{\mathrm{Cl}(n)}$ value between the maximal $Q_{\mathrm{Cl}(n)}$ and the next maximal $Q_{\mathrm{Cl}(n)}$ of the compound can be used to assess the possibility of formation of multiple dechlorination products. The compound might have multiple dechlorination products if its $\Delta Q_{\mathrm{Cl}(n)}$ is <0.01.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (no. 40730741), the China Postdoctoral Science Foundation (no. 20090450864), the Guangdong Provincial Natural Science Foundation (nos. 9351064101000001 and 8451022501000034), the Guangdong Provincial Science and Technology Planning Project (no. 2007A050100023), the Open Foundation of the State Key Lab of Environmental Geochemistry, the Fundamental Research Funds for the Central Universities (no. 2009ZM0119) and the Natural Science Foundation of South China University of Technology (no. X2HG-E5090510).

References

Adriaens P, Chang PR, Barkovskii AL. Dechlorination of PCDD/F by organic and inorganic electron transfer molecules in reduced environments. Chemosphere 1996;32:433–41.

Adrian L, Hansen SK, Fung JM, Görisch H, Zinder SH. Growth of *Dehalococcoides* strains with chlorophenols as electron acceptors. Environ Sci Technol 2007;41:2318–23.

Arulmozhiraja S, Morita M. Electron affinities and reductive dechlorination of toxic polychlorinated dibenzofurans: a density functional theory study. J Phys Chem A 2004;108:3499–508.

Becke AD. Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 1993;98:5648–53.

Bunge M, Adrian L, Kraus A, Opel M, Lorenz WG, Andreesen JR, et al. Reductive dehalogenation of chlorinated dioxins by an anaerobic bacterium. Nature 2003;421:357–60.

Choi W, Hong SJ, Chang YS, Cho Y. Photocatalytic degradation of polychlorinated dibenzo-*p*-dioxins on TiO_2 film under UV or solar light irradiation. Environ Sci Technol 2000;34:4810–5.

Fennell DE, Nijenhuis I, Wilson SF, Zinder SH, Haggblom MM. *Dehalococcoides ethenogenes* strain 195 reductively dechlorinates diverse chlorinated aromatic pollutants. Environ Sci Technol 2004;38:2075–81.

Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 03, Revision B.01. Pittsburgh PA: Gaussian Inc; 2003.

Hehre WJ, Ditchfield R, Pople JA. Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. J Chem Phys 1972;56:2257–61.

Hölscher T, Görisch H, Adrian L. Reductive dehalogenation of chlorobenzene congeners in cell extracts of *Dehalococcoides* sp. strain CBDB1. Appl Environ Microbiol 2003;69:2999–3001.

Kluyev N, Cheleptchikov A, Brodsky E, Soyfer V, Zhilnikov V. Reductive dechlorination of polychlorinated dibenzo-*p*-dioxins by zero-valent iron in subcritical water. Chemosphere 2002;46:1293–6.

Konstantinov AD, Johnston AM, Cox BJ, Petrulis JR, Orzechowski MT, Bunce NJ, et al. Photolytic method for destruction of dioxins in liquid laboratory waste and identification of the photoproducts from 2, 3, 7, 8-TCDD. Environ Sci Technol 2000;34:143–8.

Liu F, Fennell DE. Dechlorination and detoxification of 1, 2, 3, 4, 7, 8-hexachlorodibenzofuran by a mixed culture containing *Dehalococcoides ethenohenes* strain 195. Environ Sci Technol 2008;42:602–7.

Lu GN, Dang Z, Tao XQ, Yang C, Yi XY. Estimation of water solubility of polycyclic aromatic hydrocarbons using quantum chemical descriptors and partial least squares. QSAR Comb Sci 2008;27:618–26.

Lu GN, Dang Z, Fennell DE, Huang W, Li Z, Liu CQ. Rules of thumb for assessing reductive dechlorination pathways of PCDDs in specific systems. J Hazard Mater 2010;177(1–3):1145–9. doi:10.1016/j.jhazmat.2009.12.051.

Lundin L, Marklund S. Thermal degradation of PCDD/F in municipal solid waste ashes in sealed glass ampules. Environ Sci Technol 2005;39:3872–7.

Mitoma Y, Uda T, Egashira N, Simion C, Tashiro H, Tashiro M, et al. Approach to highly efficient dechlorination of PCDDs, PCDFs, and coplanar PCBs using metallic calcium in ethanol under atmospheric pressure at room temperature. Environ Sci Technol 2004;38:1216–20.

Noma Y, Mistuhara Y, Matsuyama K, Sakai S. Pathways and products of degradation of PCBs by the sodium dispersion method. Chemosphere 2007;68:871–9.

Putz MV. Density functionals of chemical bonding. Int J Mol Sci 2008a;9:1050–95.

Putz MV. Maximum hardness index of quantum acid–base bonding. MATCH Commun Math Comput Chem 2008b;60:845–68.

Putz MV. Absolute and Chemical Electronegativity and Hardness. New York, USA: Nova Publishers Inc.; 2008c.

Tao XQ, Lu GN, Fei HL, Zhou KQ. Estimation of dissolvability of chloric and alkyl benzene derivatites using quantum chemical descriptors and partial least squares. J Theor Comput Chem 2008;7:989–99.

Wang ZY, Huang WL, Fennell DE, Peng PA. Kinetics of reductive dechlorination of 1, 2, 3, 4-TCDD in the presence of zero-valent zinc. Chemosphere 2008;71:360–8.

Yang GY, Zhang XC, Wang ZY, Liu HX, Ju XH. Estimation of the aqueous solubility ($-\lg S_{\mathrm{w}}$) of all polychlorinated dibenzo-furans (PCDF) and polychlorinated dibenzo-*p*-dioxins (PCDD) congeners by density functional theory. J Mol Struct Theochem 2006;766:25–33.

Zhang XC, Yu J, Wang ZY, Liu HX. QSPR studies on $\lg K_{\mathrm{OW}}$ and $\lg K_{\mathrm{OC}}$ of fluorobenzenes and property parameters based on HF and DFT calculations. Chinese J Struct Chem 2006;25:823–9.

Zhou W, Zhai ZC, Wang ZY, Wang LS. Estimation of *n*-octanol/water partition coefficients (K_{OW}) of all PCB congeners by density functional theory. J Mol Struct Theochem 2005;755:137–45.