Journal of Hazardous Materials 177 (2010) 1145–1149

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Short communication

Rules of thumb for assessing reductive dechlorination pathways of PCDDs in specific systems

Gui-Ning Lu[a,b,c], Zhi Dang[a,d,*], Donna E. Fennell[b], Weilin Huang[a,b,*], Zhong Li[c], Cong-Qiang Liu[e]

[a] School of Environmental Science and Engineering, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, PR China
[b] Department of Environmental Sciences, Rutgers, The State University of New Jersey, 14 College Farm Road, New Brunswick, NJ 08901, United States
[c] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China
[d] The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou Higher Education Mega Center, Guangzhou 510006, PR China
[e] The State Key Lab of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, PR China

ARTICLE INFO

Article history:
Received 11 July 2009
Received in revised form
30 November 2009
Accepted 10 December 2009
Available online 21 December 2009

Keywords:
PCDD
Dechlorination pathway
DFT
Mulliken atomic charge
Chlorine atom

ABSTRACT

This paper reports a theoretical validation and proposition of the reductive dechlorination pathways for polychlorinated dibenzo-*p*-dioxin (PCDD) congeners. Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d) level for all PCDDs and Mulliken atomic charges on chlorine atoms were adopted as the probe of the dechlorination reaction activity. The experimentally substantiated dechlorination pathways of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD) and its daughter products in the presence of zero-valent zinc were validated and the complete pathway of dechlorination of octachlorodibenzo-*p*-dioxin (OCDD) was proposed. The proposed pathways were found to be consistent with anaerobic biotransformation of several PCDD congeners. Four rules of thumb arrived from this study include (1) the chlorine atoms in the longitudinal (1,4,6,9) positions are removed in preference to the chlorine atoms on lateral (2,3,7,8) positions; (2) the chlorine atom that has more neighboring chlorine atoms at *ortho*-, *meta*- and *para*-positions is to be eliminated; (3) reductive dechlorination prefers to take place on the benzene ring having more chlorine substitutions; and (4) a chlorine atom on the side of the longitudinal symmetry axis containing more chlorine atoms is preferentially eliminated. These rules of thumb can be conveniently used for rapidly predicting the major dechlorination pathway for a given PCDD in specific systems.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are persistent organic pollutants (POPs) formed primarily as byproducts during incomplete combustion process and chlorine chemical manufacturing. They are of great health and ecological concern because of their high toxicity, ubiquity in natural environments, great resistance to reactions, and high hydrophobicities [1].

Several transformation-based technologies, including photolysis, photocatalysis, γ-radiolysis, biodegradation, incineration and thermal treatment, have been developed for treating these chemicals in different systems [2–5]. Dechlorination is a major mechanism for detoxification of these chemicals [6]. Dechlorination of PCDDs using zero-valent metals has been reported [7–9] and a recent study by Wang et al. [10] reported the kinetics and detailed pathways for the reductive dechlorination of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD) with zero-valent zinc under ambient temperature and aqueous conditions. The anaerobic biotransformation pathways of 1,2,3,4-TCDD, 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (1,2,3,7,8-PeCDD) and their intermediate products have also been reported in the literature [5,11–13]. However, the reaction pathways for the majority of the 75 PCDDs have not been delineated clearly.

In fact, experimental determination of dechlorination pathways is practically difficult for some PCDDs which coelute on a GC/HPLC column. It is necessary to develop a theoretical technique to propose the dechlorination pathways and products, which use certain molecular descriptors calculated directly from chemical structures of the pollutants to indicate the eliminating activity of chlorines in different substituted positions [14]. Quantum chemical descriptors can be easily obtained by computation to clearly describe specific molecular properties for structurally related compounds, and can also provide insight into the environmental behavior of

---

* Corresponding authors at: 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 addresses: chzdang@scut.edu.cn (Z. Dang), whuang@envsci.rutgers.edu (W. Huang).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.12.051

chemicals not yet synthesized or those that cannot be examined experimentally due to their extremely hazardous nature. Hence, the application of quantum chemical descriptors in environmental chemistry is of great importance.

In this study, we used density functional theory (DFT) calculations to validate the abiotic dechlorination pathways of 1,2,3,4-TCDD and its daughter products in the presence of zero-valent zinc. The identified structure-reactivity indicator was then used to predict the main dechlorination pathways and products of octachlorodibenzo-*p*-dioxin (OCDD) and other PCDD congeners. For the convenience of discussion, we used abbreviations of MCDD, DCDD, TrCDD, TCDD, PeCDD, HxCDD, HpCDD and OCDD for PCDD congeners with 1–8 chlorines, respectively.

2. Computational method

All calculations were carried out with the Gaussian 03 program [15] running on an Intel Core 2 Duo 3.00 GHz CPU computer equipped with 5.00 GB of internal memory and the Microsoft Windows XP Professional operating system. HyperChem (Release 7.0, Hypercube Inc. 2002) was used as the molecular modeling system for constructing and viewing the molecular structures of all 75 PCDD congeners.

The constructed molecular geometry of each congener was optimized using the B3LYP hybrid functional of DFT in conjunction with 6-31G(d), a split-valence basis set with polarization function [16,17]. DFT was selected because it has been widely used in recent applications of quantum chemistry [18]. In addition, the computational time of DFT calculations is now much shorter than before since the computing speed of the personal computer has increased rapidly. The stability of molecular structures was confirmed by the vibrational frequency analysis. DFT calculations yielded dozens of structural parameters of the congeners including 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 corbon atom number in the frame), the bond length between carbon and its substituted chlorine atoms (L_n), etc. These descriptors were respectively correlated with the reported experimental dechlorination pathways of PCDDs in the presence of zero-valent zinc [10] to grope for theoretical indicator to validate the dechlorination pathways and Mulliken atomic charges on chlorine atoms were finally adopted as the probe of the dechlorination reaction activity.

3. Results and discussion

3.1. Validation of the dechlorination pathways of 1,2,3,4-TCDD and its daughter products

We used the recent laboratory study of Wang et al. [10] on abiotic dechlorination of 1,2,3,4-TCDD and its daughter products as the major database to select key structural indicators of PCDD reactivity. According to Wang et al. [10], 1,2,3,4-TCDD and 1,2,3- and 1,2,4-TrCDD were rapidly transformed in the presence of zero-valent zinc at room temperature and under aqueous condition. They proposed a detailed pathway for the reaction of 1,2,3,4-TCDD as shown in Fig. 1.

We examined the obtained structural parameters computed from DFT and found a good positive correlation between the Mulliken atomic charges for the chlorine atoms ($Q_{\mathrm{Cl}(n)}$) of PCDDs and their reactivity. Table 1 lists the $Q_{\mathrm{Cl}(n)}$ values of the three PCDDs examined in Wang et al. [10]. As can be seen in Table 1, for 1,2,3,4-TCDD, the Mulliken atomic charges on the positions 1 ($Q_{\mathrm{Cl}(1)}$) and 4 ($Q_{\mathrm{Cl}(4)}$) are 0.06413 and on the positions 2 ($Q_{\mathrm{Cl}(2)}$) and 3 ($Q_{\mathrm{Cl}(3)}$) are 0.05899. According to Fig. 1, the rates of dechlorination reactions at the positions 1 and 4 are slightly faster than at the positions 2 and 3, yielding 53% of 1,2,3-TrCDD compared to 47% of 1,2,4-TrCDD as the intermediate products. Since the difference of $Q_{\mathrm{Cl}(n)}$ between the two different positions is relatively small, the intermediate product distribution differs slightly. It does show that the chlorine atoms with the greater Mulliken atomic charges tend to be eliminated at faster rates. This trend is more obvious for the two TrCDD congeners. As shown in Table 1 and Fig. 1, the three chlorines on 1,2,3-TrCDD have Mulliken atomic charges in the order of $Q_{\mathrm{Cl}(1)}$ (0.05812) > $Q_{\mathrm{Cl}(2)}$ (0.05222) > $Q_{\mathrm{Cl}(3)}$ (0.02634), which corresponded to distributions of 88, 12 and 0% for the resulting intermediate products of DCDDs, according to Wang et al. [10]. Similarly, the three chlorine atoms on 1,2,4-TrCDD have Mulliken atomic charges in the order of $Q_{\mathrm{Cl}(1)}$ (0.05659) > $Q_{\mathrm{Cl}(4)}$ (0.03011) > $Q_{\mathrm{Cl}(2)}$ (0.02627), which corresponded to distributions of 88, 9 and 3% for the resulting intermediate products of DCDDs. Both TrCDD congeners have very large differences in $Q_{\mathrm{Cl}(n)}$ value among the three chlorine atoms. The chlorine atom with the greatest $Q_{\mathrm{Cl}(n)}$ value tends to be eliminated at the fastest rate, whereas the chlorine atom with the smallest $Q_{\mathrm{Cl}(n)}$ value tends to be eliminated at the slowest rate or does not react at all.

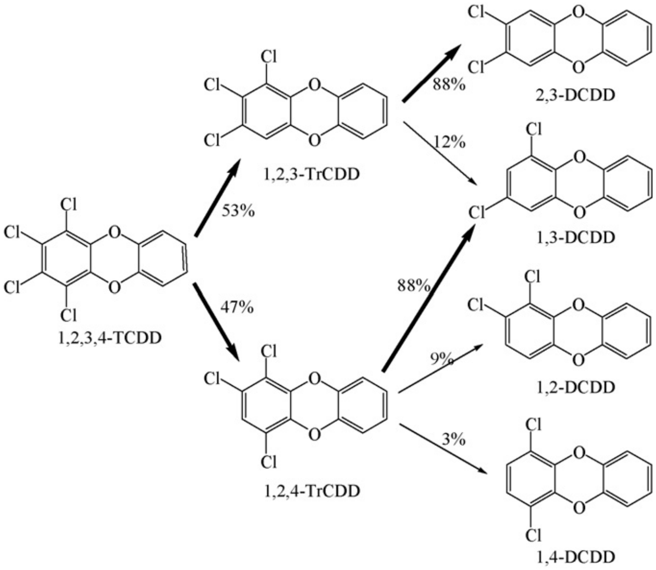

Fig. 1. The reported experimental dechlorination pathways of 1,2,3,4-TCDD and its daughter products in the presence of zero-valent zinc [10]. The major routes are marked with bold arrow. The percentages indicate the estimated ratio of the accumulated concentrations of daughter products.

3.2. Proposed pathways for the reductive dechlorination of OCDD and further validation in biotic systems

Fig. 2 presents a multistep reaction pathway for the reductive dechlorination of OCDD and its intermediate products to nontoxic dibenzo-*p*-dioxins. This pathway was proposed based solely on the positive correlation between the calculated $Q_{\mathrm{Cl}(n)}$ and the

Table 1
The Mulliken atomic charges of chlorine atoms for 1,2,3,4-TCDD and its daughter products.

Compounds	$Q_{\mathrm{Cl}(n)}$			
	1	2	3	4
1,2,3,4-TCDD	0.06413	0.05899	0.05899	0.06413
1,2,3-TrCDD	0.05812	0.05222	0.02634	
1,2,4-TrCDD	0.05659	0.02627		0.03011

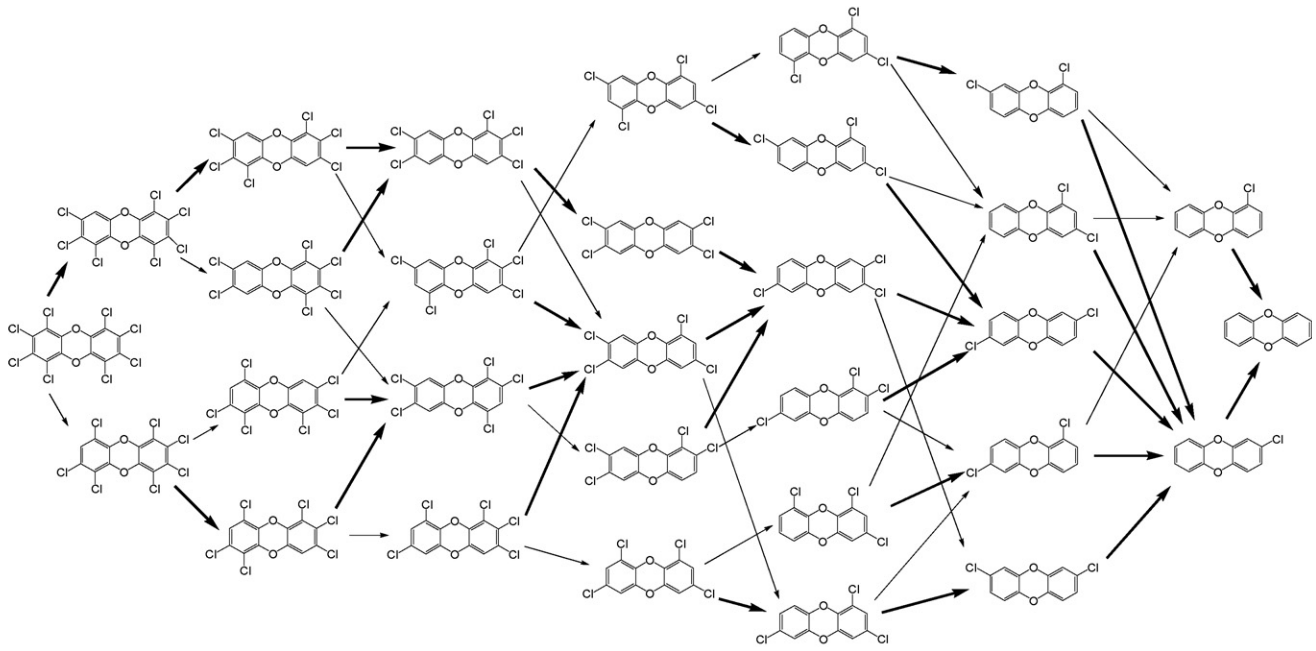

Fig. 2. Proposed ruductive dechlorination pathways for OCDD and its intermediate products. The major routes are marked with bold arrow and the secondary routes are marked with thin arrow.

Table 2
Selected Mulliken atomic charges of chlorine atoms for all PCDDs.

Compound[a]	$Q_{\mathrm{Cl}(n)}$[b]		$Q_{\mathrm{Cl}(n)}$[c]		Compound[a]	$Q_{\mathrm{Cl}(n)}$[b]		$Q_{\mathrm{Cl}(n)}$[c]	
	n	Value	n	Value		n	Value	n	Value
1	1	0.00827			1278	1	0.05739	8	0.02691
2	2	−0.01973			1279	1	0.06454	9	0.03919
12	1	0.04900	2	0.01430	1289	1	0.06443	2	0.02157
13	1	0.02365	3	−0.00621	1368	1	0.03258	3	0.00307
14	1	0.01795			1369	1	0.03906	9	0.03376
16	1	0.01279			1378	1	0.03256	8	0.02762
17	1	0.01348	7	−0.01510	1379	1	0.03935	3	0.00217
18	1	0.01467	8	−0.01421	1469	1	0.03345		
19	1	0.02120			1478	7	0.02726	1	0.02690
23	2	0.01868			2378	2	0.02650		
27	2	−0.01471			12346	4	0.07613	1	0.06699
28	2	−0.01461			12347	4	0.06891	1	0.06765
123	1	0.05812	2	0.05222	12367	1	0.06432	6	0.05962
124	1	0.05659	4	0.03011	12368	1	0.06621	2	0.05948
126	1	0.05251	2	0.01840	12369	1	0.07326	2	0.05893
127	1	0.05324	2	0.01879	12378	1	0.06606	2	0.05914
128	1	0.05449	2	0.01881	12379	1	0.07342	2	0.05917
129	1	0.06126	9	0.02487	12389	1	0.07335	9	0.06684
136	1	0.02735	6	0.01826	12467	6	0.06672	1	0.06220
137	1	0.02810	3	−0.00142	12468	1	0.06418	4	0.04535
138	1	0.02935	3	−0.00165	12469	1	0.07124	4	0.04492
139	1	0.03577	9	0.02508	12478	1	0.06413	4	0.03853
146	4	0.03024	6	0.02498	12479	1	0.07148	9	0.04229
147	4	0.02372	1	0.02241	12489	1	0.07172	9	0.06744
236	3	0.02363	2	0.02264	123467	4	0.07894	1	0.06961
237	3	0.02327	2	0.02306	123468	4	0.07895	1	0.07147
1234	1	0.06413	2	0.05899	123469	1	0.07867	2	0.06541
1236	1	0.06145	2	0.05585	123478	1	0.07165	2	0.06564
1237	1	0.06214	2	0.05598	123678	1	0.06807	2	0.06155
1238	1	0.06331	2	0.05605	123679	1	0.07547	6	0.06604
1239	1	0.07030	2	0.05558	123689	1	0.07588	9	0.07398
1246	1	0.05942	4	0.04203	123789	1	0.07561	2	0.06110
1247	1	0.06022	4	0.03559	124679	1	0.07367	4	0.04795
1248	1	0.06141	4	0.03426	124689	1	0.07421	4	0.04742
1249	1	0.06847	4	0.03345	1234678	4	0.08103	6	0.07735
1267	1	0.05566	2	0.02174	1234679	4	0.08122	1	0.08068
1268	1	0.05753	6	0.03082	12346789	1	0.08258	2	0.06960
1269	1	0.06462	9	0.03364					

[a] Given are the substitution position of the PCDD congener.
[b] Given are the maximal Q_{Cl} values.
[c] Given are the secondary maximal Q_{Cl} values, not including the positions equal to the maximal.

reactivity of the three PCDDs delineated above and the $Q_{Cl(n)}$ data shown in Table 2. As shown in Fig. 2, the major pathway for OCDD dechlorination should follow OCDD → 1,2,3,4,6,7,8-HpCDD → 1,2,3,6,7,8-HxCDD → 1,2,3,7,8-PeCDD → 2,3,7,8-TCDD → 2,3,7-TrCDD → 2,7-DCDD → 2-MCDD → DD. This pathway is indeed not environmentally friendly as the less chlorinated intermediate products with four lateral chlorines are more toxic [19]. The theoretical study by Zhao et al. [20] also shown that 1,2,3,7,8-PeCDD had high likelihood of obtaining reductive dechlorination products more toxic than the parent species. The proposed pathway shown in Fig. 2 is indeed consistent with a laboratory study of PCDD biotransformation. Barkovskii and Adriaens [21] used a microcosm technique to monitor anaerobic biodegradation of PCDDs associated with the Passaic River sediments. They found *peri*-dechlorination pathway of 2,3,7,8-substituted HpCDD to PeCDDs and to 2,3,7,8-TCDD transformed by a microbial consortium [21].

The dechlorination pathways of PCDDs may be different under different environmental conditions. Studies have shown various dechlorination mechanisms for 1,2,3,4-TCDD in different systems [5,11–13]. It should be noted that the proposed main dechlorination pathways using $Q_{Cl(n)}$ for some PCDD congeners are consistent with biotranformation studies [11–13]. Bunge et al. [11] used an anaerobic bacterium *Dehalococcoides* sp. strain CBDB1 to dechlorinate 1,2,3,4-TCDD and 1,2,3,7,8-PeCDD. Their reported reaction pathways for these two PCDDs and their intermediate products (including 1,3,7,8- and 2,3,7,8-TCDD, 1,2,3-, 1,2,4- and 2,3,7-TrCDD, 1,3- and 2,3-DCDD) were exactly the same as our predictions. Meanwhile, we further found the biotransformation pathways of chlorobenzene and chlorophenol congeners conducted by *Dehalococcoides* sp. strain CBDB1 also can be predicted by $Q_{Cl(n)}$ (data not shown) [22,23]. Ballerstedt et al. [12] found that the major intermediates of 1,2,4-TrCDD by an anaerobic consortium isolated from the Saale river sediment was 1,3-DCDD, whereas 2,3-DCDD was the major intermediate and 1,3-DCDD was the minor for the dechlorination of 1,2,3-TrCDD. 2-MCDD was detected as the major product from 1,3- and 2,3-DCDD. These product distributions reported by Ballerstedt et al. [12] were consistent with the reaction pathways predicted with our theoretical approach. The major biotranformation pathways for 1,2,4-TrCDD, 1,3- and 2,3-DCDD delineated by Beurskens et al. [13] also supported our proposal.

One exception to our theoretical predictions using $Q_{Cl(n)}$ is the biotic transformation pathway of 1,2,3,4-TCDD reported by Fennell et al. [5]. In that study, *Dehalococcoides ethenogenes* strain 195 was shown to degrade 1,2,3,4-TCDD to form 1,2,4-TrCDD, but not 1,2,3-TrCDD, as the sole daughter product. It is likely that the mechanisms for reductive dechlorination by this specific strain may be very different. Further study on this deviation is needed. Other chlorinated aromatic pollutants such as polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and chlorobenzenes might be tackled similarly as PCDDs and the probe might be used for proposing the dechlorination pathways of them in the same system. However, this hypothesis should to be tested using more experimental data to insure its universality.

3.3. *Four rules of thumb for predicting major pathways of PCDD dechlorination*

Four rules of thumb for predicting major pathways of PCDD dechlorination can be drawn from the information presented in Figs. 1 and 2 and the $Q_{Cl(n)}$ data shown in Table 2. The first rule of thumb is that the chlorine atoms in the longitudinal (1,4,6,9) positions are preferentially eliminated as compared to the chlorine atoms on the lateral (2,3,7,8) positions. The second general rule drawn from our analysis is the steric effect, i.e., among several chlorine atoms, the one most crowded by *ortho*-, *meta*- and *para*-substituted chlorines is preferentially eliminated (the positions 1 and 9, 4 and 6 are considered as *meta*-position, respectively). When used for predicting reaction pathways, the second rule should obey the first rule. Using these two rules in order, we can simply and swiftly propose the major dechlorination reaction pathways of any PCDD congeners.

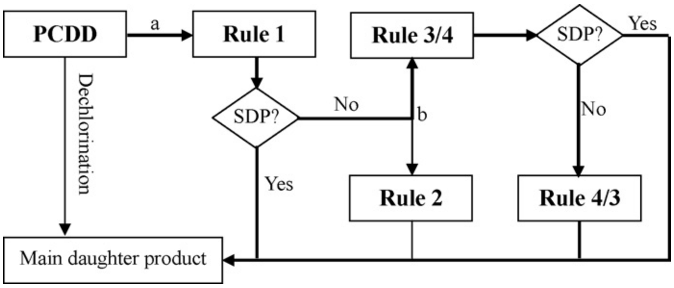

Fig. 3. Scheme of the application order of the rules of thumb. SDP stands for sole daughter product, the bold route is suggested the fastest proposing order. (a) For 2,3,6-TrCDD and 1,4,7,8-TCDD, overleap Rule 1 and go to the next step directly and (b) 1,2,4,6,7-PeCDD does not obey Rule 3 and can only go down to Rule 2, see detail in the text for these exceptions.

An example of the first rule is that the chlorine atom on position 1 of 1,2,3-TrCDD and 1,2,3,7-TCDD is eliminated more easily than the chlorines on the other positions. Better examples for applications of the second rule are that the chlorine atom on position 1 is preferentially eliminated from 1,2,6,9-TCDD and 1,2,3,6,8,9-HxCDD, and that position 4 chlorine is removed favorably from 1,4,7-TrCDD and 1,2,3,4,7-PeCDD. Among all 75 PCDD congeners, two exceptions were found for the first rule: 2,3,6-TrCDD and 1,4,7,8-TCDD, which have the largest $Q_{Cl(n)}$ values on the lateral positions that they might not preferentially eliminate chlorine atoms in the longitudinal positions. However, they obey the second rule. Our calculations showed that 2,3,6-TrCDD has $Q_{Cl(3)}$ (0.02363) > $Q_{Cl(2)}$ (0.02264) > $Q_{Cl(6)}$ (0.01817) and 1,4,7,8-TCDD has $Q_{Cl(7)} = Q_{Cl(8)}$ (0.02726) > $Q_{Cl(1)} = Q_{Cl(4)}$ (0.02690). For each of these two congeners, the computed $Q_{Cl(n)}$ values and their differences among the chlorine atoms are very small compared to other congeners. In these cases, they should not have large difference on the distribution of daughter products.

According to the above Rule 2, we can further generalize two additional rules of thumb for predicting reductive dechlorination pathways. When a PCDD congener has chlorine substitutions on both benzene ring structures, dechlorination prefers to take place on the benzene ring having more chlorine substitutions (Rule 3). As shown in Fig. 2, the first step of the reductive dechlorination of 1,2,3,4,6,7,8-HpCDD and 1,2,3,6,8-PeCDD follows this generalization. The only exception found for this rule is for 1,2,4,6,7-PeCDD, which prefers elimination of the chlorine on position 6, however, such an exception can be predicted by Rule 2. Meanwhile, when the positions of chlorine atoms on a PCDD structure are grouped to two sides (1,2,8,9 versus 3,4,6,7) divided by its longitudinal axis of symmetry, a chlorine atom on the side containing more chlorine atoms is preferentially eliminated (Rule 4). For example, chlorines on position 4 of 1,4,6-TrCDD and position 1 of 1,2,4,8-TCDD favor elimination in the first step of reductive dechlorination.

Since Rule 3 and Rule 4 are inferences of Rule 2 and more visual than Rule 2, we can use the combination of Rule 1 + 3 and/or 4 to propose the major dechlorination reaction pathways of PCDD congeners. The application orders of these rules are shown in Fig. 3.

4. Conclusion

We proposed a complete main pathway for reductive dechlorination of PCDD congeners based on the B3LYP/6-31G(d) method.

This proposed pathway was validated with literature data on abiotic and biotic reductive dechlorination of PCDDs. According to the theoretical computation and experimental validation results, we summarized two rules of thumb and two generalizations for predicting the main dechlorination pathways of any PCDD congeners in specific systems. These rules are not only satisfactory in the abiotic zero-valent zinc system, but also are satisfactory in some biotic systems like specific microorganisms, however, they need to be further validated by more experinmental data.

Acknowledgements

The work was supported by the National Science Foundation of China (No. 40730741), the Guangdong Provincial Natural Science Foundation (No. 9351064101000001) and the Open Foundation of the State Key Lab of Environmental Geochemistry to ZD, the China Postdoctoral Science Foundation (No. 20090450864) and the Doctorate Foundation of SCUT to GNL. It was also partially funded by the US National Science Foundation with an SGER grant (BES-0636820) to WH, and the SERDP of the DoD with a grant to DEF.

References

[1] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Chlorinated Dibenzo-p-Dioxins, US Department of Health and Human Services, Public Health Service, Atlanta, GA, 1998.

[2] L. Lundin, S. Marklund, Thermal degradation of PCDD/F in municipal solid waste ashes in sealed glass ampules, Environ. Sci. Technol. 39 (2005) 3872–3877.

[3] A.D. Konstantinov, A.M. Johnston, B.J. Cox, J.R. Petrulis, M.T. Orzechowski, N.J. Bunce, C.H.M. Tashiro, B.G. Chittim, Photolytic method for destruction of dioxins in liquid laboratory waste and identification of the photoproducts from 2,3,7,8-TCDD, Environ. Sci. Technol. 34 (2000) 143–148.

[4] W. Choi, S.J. Hong, Y.S. Chang, Y. Cho, Photocatalytic degradation of polychlorinated dibenzo-*p*-dioxins on TiO_2 film under UV or solar light irradiation, Environ. Sci. Technol. 34 (2000) 4810–4815.

[5] D.E. Fennell, I. Nijenhuis, S.F. Wilson, S.H. Zinder, M.M. Haggblom, *Dehalococcoides ethenogenes* strain 195 reductively dechlorinates diverse chlorinated aromatic pollutants, Environ. Sci. Technol. 38 (2004) 2075–2081.

[6] H. Fueno, K. Tanaka, S. Sugawa, Theoretical study of the dechlorination reaction pathways of octachlorodibenzo-*p*-dioxin, Chemosphere 48 (2002) 771–778.

[7] P. Adriaens, P.R. Chang, A.L. Barkovskii, Dechlorination of PCDD/F by organic and inorganic electron transfer molecules in reduced environments, Chemosphere 32 (1996) 433–441.

[8] N. Kluyev, A. Cheleptchikov, E. Brodsky, V. Soyfer, V. Zhilnikov, Reductive dechlorination of polychlorinated dibenzo-*p*-dioxins by zero-valent iron in subcritical water, Chemosphere 46 (2002) 1293–1296.

[9] Y. Mitoma, T. Uda, N. Egashira, C. Simion, H. Tashiro, M. Tashiro, X. Fan, 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. 38 (2004) 1216–1220.

[10] Z.Y. Wang, W.L. Huang, D.E. Fennell, P.A. Peng, Kinetics of reductive dechlorination of 1,2,3,4-TCDD in the presence of zero-valent zinc, Chemosphere 71 (2008) 360–368.

[11] M. Bunge, L. Adrian, A. Kraus, M. Opel, W.G. Lorenz, J.R. Andreesen, H. Görisch, U. Lechner, Reductive dehalogenation of chlorinated dioxins by an anaerobic bacterium, Nature 421 (2003) 357–360.

[12] H. Ballerstedt, A. Kraus, U. Lechner, Reductive dechlorination of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin and its products by anaerobic mixed cultures from Saale River sediment, Environ. Sci. Technol. 31 (1997) 1749–1753.

[13] J.E.M. Beurskens, M. Toussaint, J. de Wolf, J.M.D. van der Steen, P.C. Slot, L.C.M. Commandeur, J.R. Parsons, Dehalogenation of chlorinated dioxins by an anaeroic microbial consortium from sediment, Environ. Toxicol. Chem. 14 (1995) 939–943.

[14] M.M. Lynam, M. Kuty, J. Damborsky, J. Koca, P. Adriaens, Molecular orbital calculations to describe microbial reductive dechlorination of polychlorinated dioxins, Environ. Toxicol. Chem. 17 (1998) 988–997.

[15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al., Gaussian 03, Revision B.01, Gaussian Inc., Pittsburgh, PA, 2003.

[16] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5653.

[17] W.J. Hehre, R. Ditchfield, J.A. Pople, 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. 56 (1972) 2257–2261.

[18] G.N. Lu, Z. Dang, X.Q. Tao, C. Yang, X.Y. Yi, Estimation of water solubility of polycyclic aromatic hydrocarbons using quantum chemical descriptors and partial least squares, QSAR Comb. Sci. 27 (2008) 618–626.

[19] A. Poland, J.C. Knutson, 2,3,7,8-Tetrachlorodibenzo-thorn-dioxin and related halogenated aromatic hydrocarbons: examination of the mechanism of toxicity, Annu. Rev. Pharmacol. Toxicol. 22 (1982) 517–554.

[20] Y.Y. Zhao, F.M. Tao, E.Y. Zeng, Structures, reductive dechlorination, and electron affinities of selected polychlorinated dibenzo-*p*-dioxins: density functional theory study, J. Phys. Chem. A 111 (2007) 11638–11644.

[21] A.L. Barkovskii, P. Adriaens, Microbial dechlorination of historically present and freshly spiked chlorinated dioxins and diversity of dioxin-dechlorinating populations, Appl. Environ. Microbiol. 62 (1996) 4556–4562.

[22] L. Adrian, S.K. Hansen, J.M. Fung, H. Görisch, S.H. Zinder, Growth of *Dehalococcoides* strains with chlorophenols as electron acceptors, Environ. Sci. Technol. 41 (2007) 2318–2323.

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