Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Mechanistic insight into Dehalococcoides-mediated reductive dechlorination of polychlorinated biphenyls

Shangwei Zhang,*[ab] Wei Ouyang,[ab] Xinghui Xia,[b] Wu Wen, *[c] Lorenz Adrian,[de] and Gerrit Schüürmann[fg]

[a]Advanced Interdisciplinary Institute of Environment and Ecology, Beijing Normal University, Zhuhai, 519087, China

[b]State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing, 100875 China

[c]Instrumentation and Service Centre for Science and Technology, Beijing Normal University, Zhuhai, 519087, China

[d]UFZ Department of Environmental Biotechnology, Helmholtz Centre for Environmental Research, Permoserstraße 15, 04318 Leipzig, Germany

[e]Chair of Geobiotechnology, Technische Universität Berlin, Ackerstraße 76, 13355 Berlin, Germany

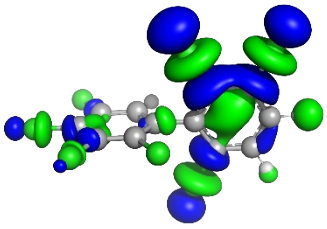
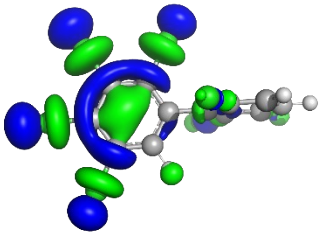
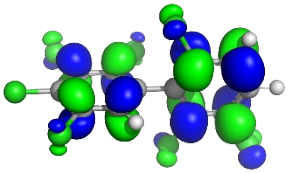
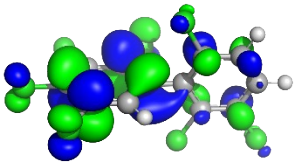
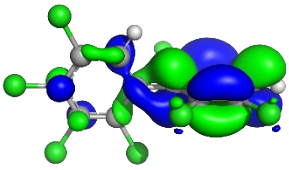
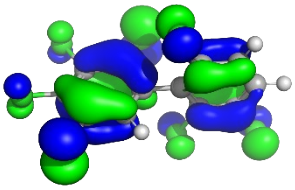
[f]UFZ Department of Ecological Chemistry, Helmholtz Centre for Environmental Research, Permoserstraße 15, 04318 Leipzig, Germany

[g]Technical University Bergakademie Freiberg, Institute of Organic Chemistry, Leipziger Straße 29, 09596 Freiberg, Germany

*Correspondence should be addressed to S. Z. (E-mail: zhangshangwei@bnu.edu.cn, shangwei.zhang@ufz.de) and W. W. (wenwuliwen@bnu.edu.cn)

Table of Contents

Table S1 Key molecular orbitals (MO) of 2345-236-CB[a]

orbital position	orbital shape	orbital position	orbital shape
LUMO+5		LUMO+4	
LUMO+3		LUMO+2	
LUMO+1		LUMO	
HOMO			

[a] Key molecular orbitals calculated at spin-unrestricted BP86/Def2TZVPP//BP86/Def2SVP covers two frontier MOs (HOMO and LUMO) and five energy-lowest unoccupied MOs (LUMO+1 ··· LUMO+5). The structure of 2345-236-PCB is represented by balls and sticks. The blue and green isosurfaces of MOs are depicted at isovalues of 0.03 and -0.03, respectively.

Table S2 The contributions of natural bond orbital (NBO) to molecular orbital (MO)[a]

compound	MO	NBO contribution to MO		
		contribution coefficient	NBO	contribution (%)
cob(I)alamin	HOMO	0.961	[76]: LP (1)Co 1(lp)	92.4
234-236-PCB	LUMO+4	0.466	[104]: BD*(1) C 8-Cl 9*	21.7
		0.453	[102]: BD*(1) C 6-Cl 7*	20.5
		0.409	[90]: BD*(1)Cl 1- C 2*	16.7
		-0.31	[118]: BD*(1) C17-Cl18*	9.61
		-0.246	[115]: BD*(1) C15-Cl16*	6.05
		-0.231	[108]: BD*(1) C11-Cl12*	5.34
2345-236-PCB	LUMO+4	0.489	[124]: BD*(1) C16-Cl17*	23.9
		0.470	[121]: BD*(1) C14-Cl15*	22.1
		0.390	[126]: BD*(1) C18-Cl19*	15.2
		0.381	[119]: BD*(1) C12-Cl13*	14.5

[a] The molecular orbital decomposition to natural bond orbital were done by NBO 6.0 implanted in Gaussian Rev 09 D.01 at theoretical level of spin-unrestricted BP86/Def2TZVPP//BP86/Def2SVP.

Table S3 The oxidation states of cobalt and other elements for species along reaction coordinates of configuration specific route, Cl_3-234Ar-a_2 of 234-236-CB[a]

atom number (atom)	RC	TS	IM	PC
1(Co)	1	3	3	2
2(N)	-3	-3	-3	-3
3(N)	-3	-3	-3	-3
4(N)	-3	-3	-3	-3
5(N)	-3	-3	-3	-3
6(C)	0	0	0	0
7(C)	0	0	0	0
8(C)	4	4	4	4
9(C)	4	4	4	4
10(C)	4	4	4	4
11(O)	-2	-2	-2	-2
12(C)	4	4	4	4
13(C)	4	4	4	4
14(C)	4	4	4	4
15(C)	4	4	4	4
16(C)	4	4	4	4
17(C)	4	4	4	4
18(C)	2	2	2	2
19(C)	4	4	4	4
20(C)	4	4	4	4
21(C)	4	4	4	4
22(C)	4	4	4	4
23(C)	4	4	4	4
24(C)	4	4	4	4
25(C)	4	4	4	4
26(C)	4	4	4	4
27(C)	4	4	4	4
28(C)	-1	-1	1	3
29(C)	1	0	0	1
30(C)	3	3	4	1
31(C)	4	4	4	4
32(O)	-2	-2	-2	-2
33(N)	-3	-3	-3	-3
34(C)	3	4	3	3
35(C)	4	4	3	3
36(C)	4	4	4	4
37(N)	-3	-3	-3	-3
38(O)	-2	-2	-2	-2
39(C)	1	2	0	1
40(C)	1	0	0	1
41(C)	4	4	2	3
42(C)	4	4	4	4
43(O)	-2	-2	-2	-2
44(N)	-3	-3	-3	-3
45(C)	4	4	4	3
46(C)	2	1	2	2
47(C)	4	4	4	4

48(O)	-2	-2	-2	-2
49(N)	-3	-3	-3	-3
50(C)	-2	-2	-2	-2
51(C)	1	1	1	2
52(C)	4	2	3	3
53(C)	4	4	4	4
54(C)	4	4	4	4
55(O)	-2	-2	-2	-2
56(N)	-3	-3	-3	-3
57(C)	2	3	1	0
58(C)	-1	0	-1	-2
59(C)	4	4	4	2
60(C)	4	4	3	4
61(C)	4	4	4	4
62(O)	-2	-2	-2	-2
63(N)	-3	-3	-3	-3
64(C)	4	3	4	3
65(C)	4	4	4	4
66(N)	-3	-3	-3	-3
67(O)	-2	-2	-2	-2
68(H)	1	1	1	1
69(H)	1	1	1	1
70(H)	1	1	1	1
71(H)	1	1	1	1
72(H)	1	1	1	1
73(H)	1	1	1	1
74(H)	1	1	1	1
75(H)	1	1	1	1
76(H)	1	1	1	1
77(H)	1	1	1	1
78(H)	1	1	1	1
79(H)	1	1	1	1
80(H)	1	1	1	1
81(H)	1	1	1	1
82(H)	1	1	1	1
83(H)	1	1	1	1
84(H)	1	1	1	1
85(H)	1	1	1	1
86(H)	1	1	1	1
87(H)	1	1	1	1
88(H)	1	1	1	1
89(H)	1	1	1	1
90(H)	1	1	1	1
91(H)	1	1	1	1
92(H)	1	1	1	1
93(H)	1	1	1	1
94(H)	1	1	1	1
95(H)	1	1	1	1
96(H)	1	1	1	1
97(H)	1	1	1	1
98(H)	1	1	1	1
99(H)	1	1	1	1
100(H)	1	1	1	1

101(H)	1	1	1	1
102(H)	1	1	1	1
103(H)	1	1	1	1
104(H)	1	1	1	1
105(H)	1	1	1	1
106(H)	1	1	1	1
107(H)	1	1	1	1
108(H)	1	1	1	1
109(H)	1	1	1	1
110(H)	1	1	1	1
111(H)	1	1	1	1
112(H)	1	1	1	1
113(H)	1	1	1	1
114(H)	1	1	1	1
115(H)	1	1	1	1
116(H)	1	1	1	1
117(H)	1	1	1	1
118(H)	1	1	1	1
119(H)	1	1	1	1
120(H)	1	1	1	1
121(H)	1	1	1	1
122(H)	1	1	1	1
123(H)	1	1	1	1
124(H)	1	1	1	1
125(H)	1	1	1	1
126(H)	1	1	1	1
127(H)	1	1	1	1
128(H)	1	1	1	1
129(H)	1	1	1	1
130(H)	1	1	1	1
131(H)	1	1	1	1
132(H)	1	1	1	1
133(H)	1	1	1	1
134(H)	1	1	1	1
135(H)	1	1	1	1
136(H)	1	1	1	1
137(H)	1	1	1	1
138(C)	2	2	2	2
139(C)	2	2	2	2
140(C)	2	2	2	2
141(C)	2	2	2	2
142(C)	2	2	2	2
143(C)	4	4	4	4
144(O)	-2	-2	-2	-2
145(H)	1	1	1	1
146(H)	1	1	1	1
147(H)	1	1	1	1
148(H)	1	1	1	1
149(H)	1	1	1	1
150(H)	1	1	1	1
151(Cl)	-1	-1	-1	-1
152(C)	4	2	2	2
153(C)	4	4	4	4

154(C)	4	4	4	4
155(C)	4	4	4	4
156(C)	2	2	2	2
157(C)	2	2	2	2
158(C)	4	4	4	4
159(H)	1	1	1	1
160(C)	4	4	4	4
161(C)	4	4	4	4
162(C)	4	4	4	4
163(C)	2	2	2	2
164(C)	2	2	2	2
165(Cl)	-1	-1	-1	-1
166(Cl)	-1	-1	-1	-1
167(Cl)	-1	-1	-1	-1
168(Cl)	-1	-1	-1	-1
169(H)	1	1	1	1
170(H)	1	1	1	1
171(H)	1	1	1	1
172(Cl)	-1	-1	-1	-1

[a] The oxidation states of all species are calculated at spin-unrestricted BP86/Def2TZVPP//BP86/Def2SVP according to localized orbital bonding method. The oxidation states of Co in RC, TS, IM, an PC at other configuration-specific reaction routes are the same as their counterparts here and thus are not given.

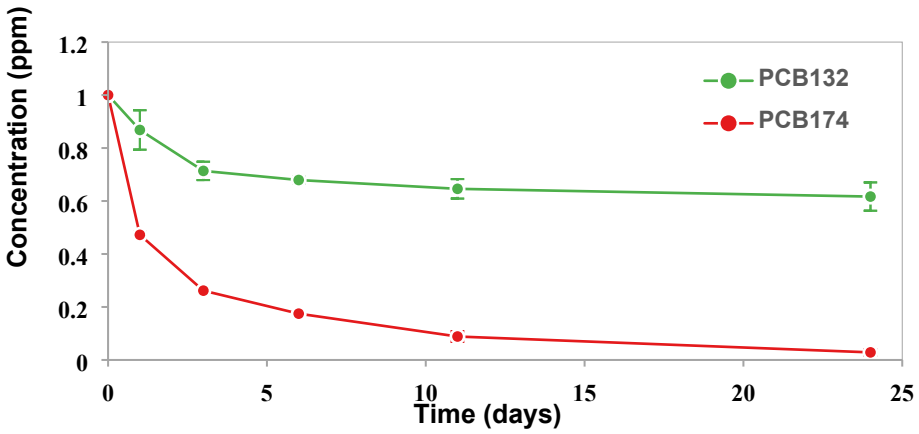


Fig. S1 Reductive dechlorination kinetics of PCB132 (234-236-CB) and PCB174 (2345-236-CB) with *Dehalococcoides mccartyi* strain CG1. The data was obtained from reference [1].

References

[1] L. Yu, Q. Lu, L. Qiu, G. Xu, Y. Zeng, X. Luo, S. Wang and B. Mai, Applied Environmental Microbiology, 2018, 84, e01300-01318.