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Compound specific stable isotope analysis (CSIA) to characterize transformation mechanisms of α-hexachlorocyclohexane

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Outline

- Introduction
- Experimental
- Results
- Discussion
- Conclusion

Introduction

Background

Hexachlorocyclohexane (HCH) isomers have been listed in the Stockholm Convention on Persistent Organic Pollutants (POPs)

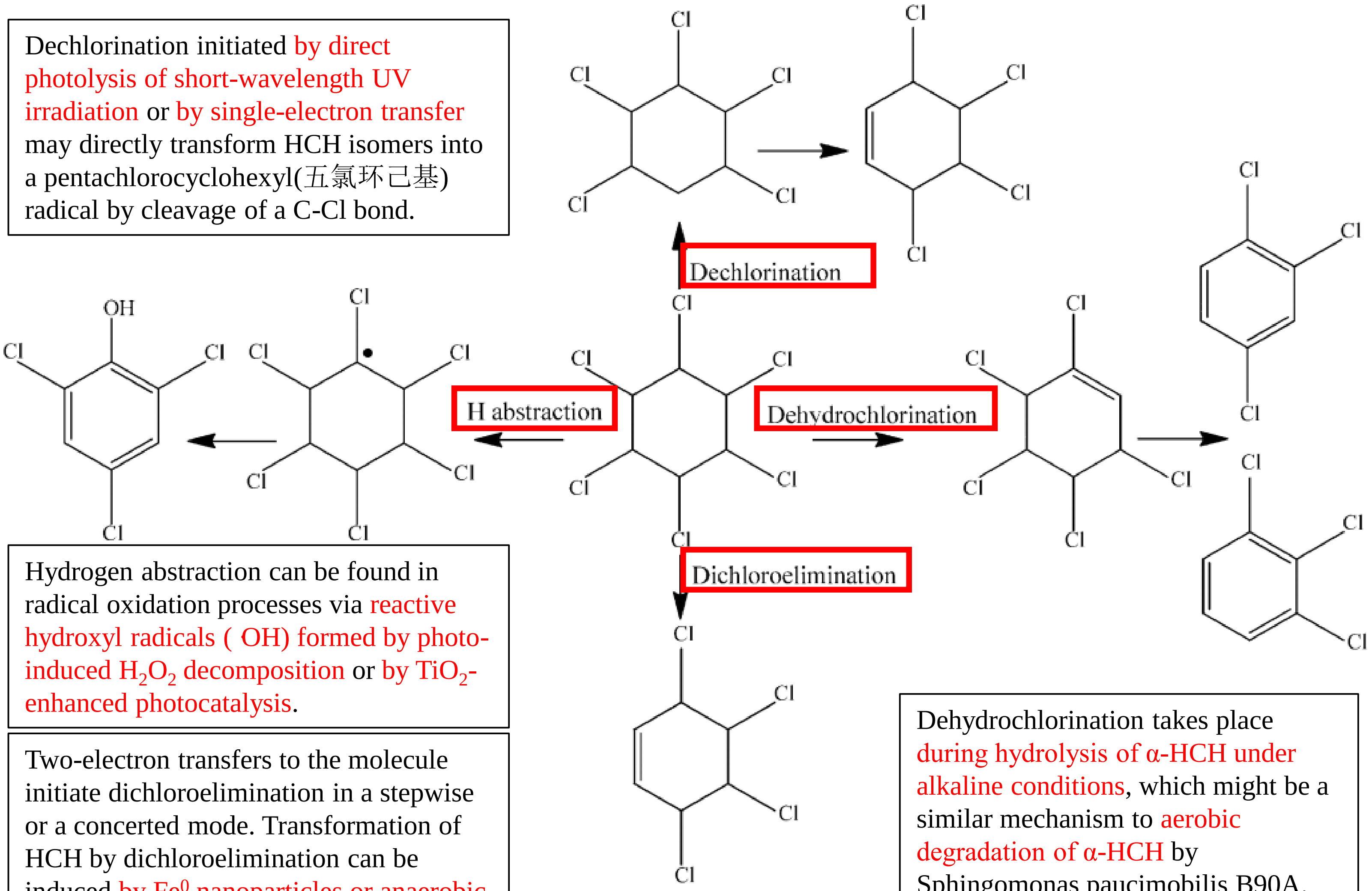
Although production of HCH is mostly banned, residues from previous applications, improper waste disposal and storage require long-term monitoring in order to assess HCH sources and sinks.

Technical-grade HCH, an important insecticide formulation in agriculture, forestry, and wood preservative, consists mainly of five major isomers: α(60-70%), β(5-12%), γ(10-12%), δ (6-10%) and ε(3-4%).

Understanding of the fate of α-HCH is of great importance for long-term cleanup activities.

Introduction

Transformation pathways of α-HCH in biological and chemical processes



Dechlorination initiated by direct photolysis of short-wavelength UV irradiation or by single-electron transfer may directly transform HCH isomers into a pentachlorocyclohexyl(五氯环己基) radical by cleavage of a C-Cl bond.

Hydrogen abstraction can be found in radical oxidation processes via reactive hydroxyl radicals (OH) formed by photo-induced H_2O_2 decomposition or by TiO_2-enhanced photocatalysis.

Two-electron transfers to the molecule initiate dichloroelimination in a stepwise or a concerted mode. Transformation of HCH by dichloroelimination can be induced by Fe^0 nanoparticles or anaerobic degradation of α-HCH.

Dehydrochlorination takes place during hydrolysis of α-HCH under alkaline conditions, which might be a similar mechanism to aerobic degradation of α-HCH by Sphingomonas paucimobilis B90A.

Introduction

Biological and chemical transformation processes :

a. Aerobic and anaerobic microbial degradation

Biological processes

b. Hydrolysis

c. Radical oxidation by photo-Fentonprocess or by photocatalytic degradation

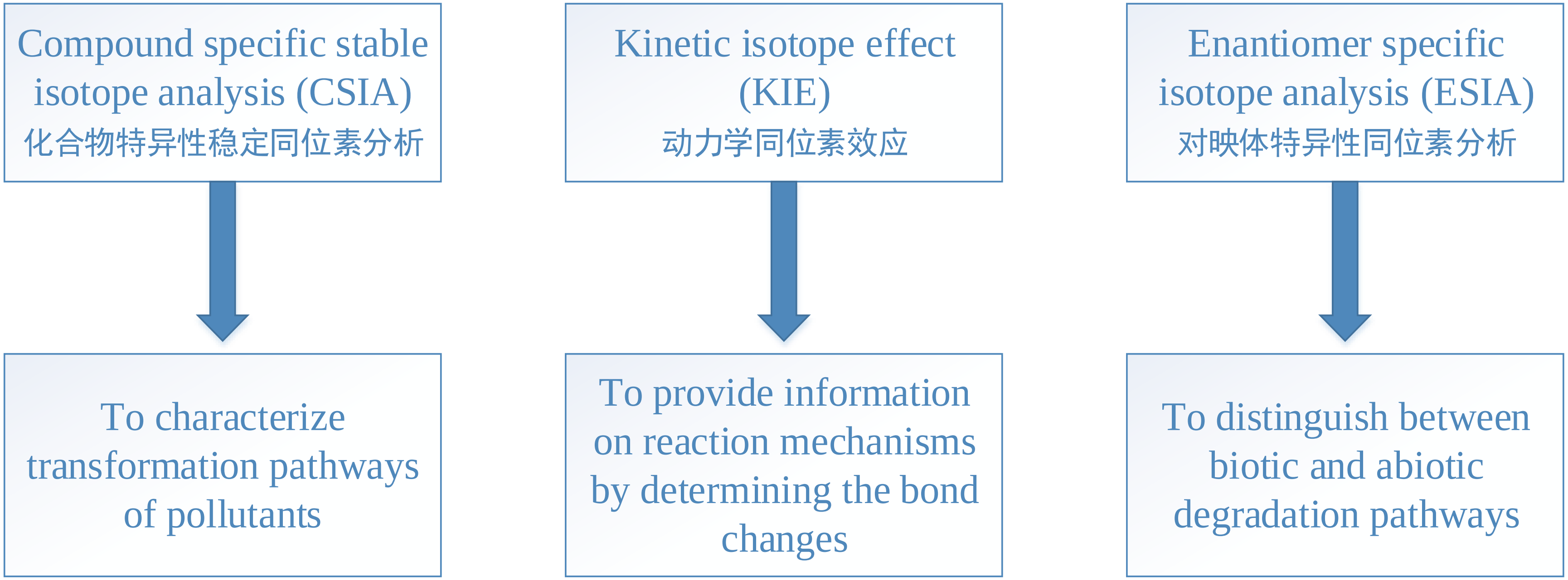
d. Electrochemical reduction

e. Nanoscale zero-valent iron (Fe^0) induced reduction

Chemical processes

Introduction

Information on the transformation mechanism



Compound specific stable isotope analysis (CSIA)
化合物特异性稳定同位素分析

To characterize transformation pathways of pollutants

Kinetic isotope effect (KIE)
动力学同位素效应

To provide information on reaction mechanisms by determining the bond changes

Enantiomer specific isotope analysis (ESIA)
对映体特异性同位素分析

To distinguish between biotic and abiotic degradation pathways

Experimental

Transformation methods

Analytical methods

Experiment

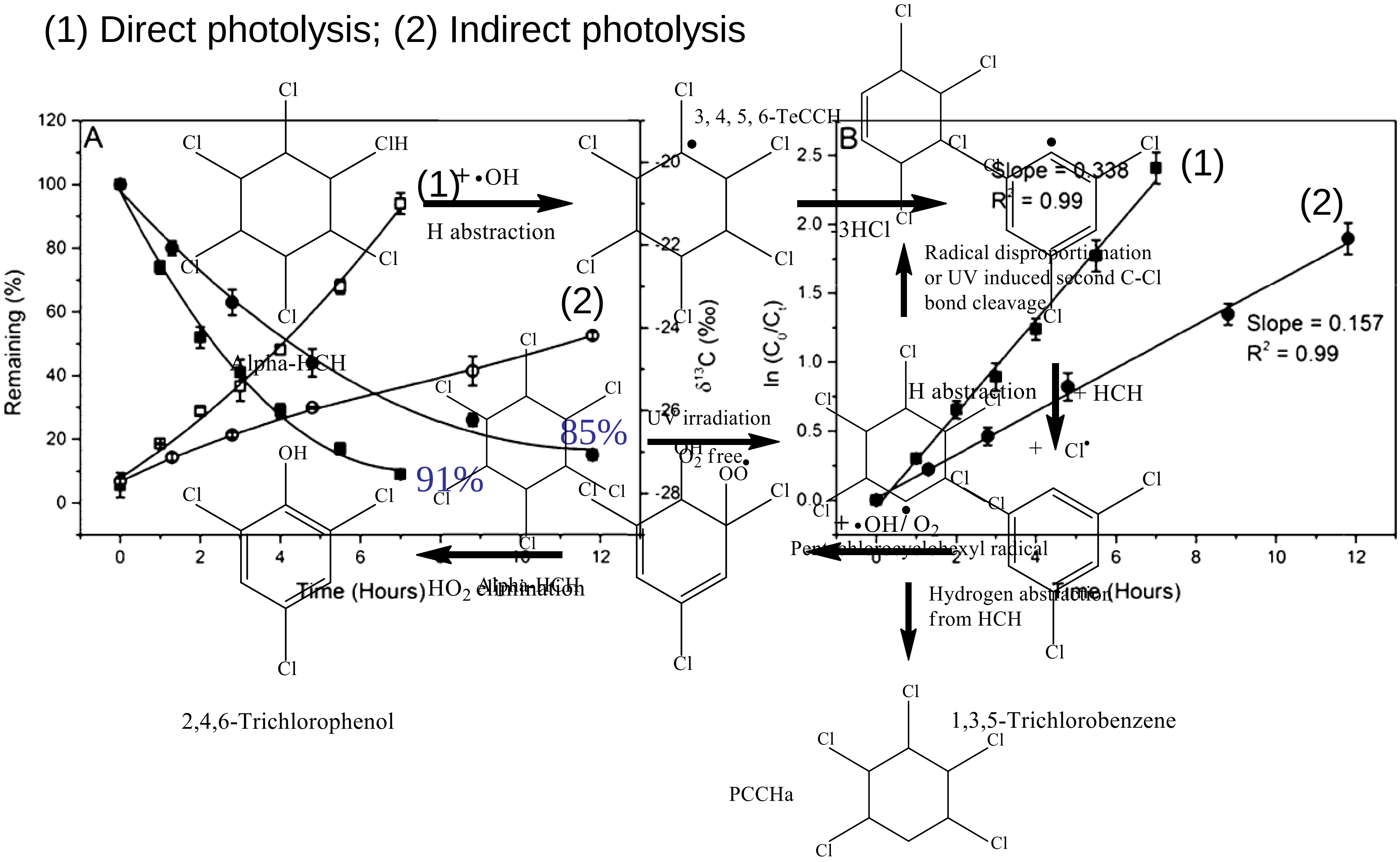
- Direct and indirect photolysis
- Alkaline hydrolysis
- Electrochemical reduction
- Reduction by Fe0 nanoparticles

- GC-FID: the concentration of α-HCH
- GC–MS: degradation products
- GC-C-IRMS: carbon stable isotope ratios of α-HCH
- Modified cyclodextrin (CD) with a Gamma DEXTM 120 chiral column : isotopic composition of individual enantiomers referred as ESIA of α-HCH

Result

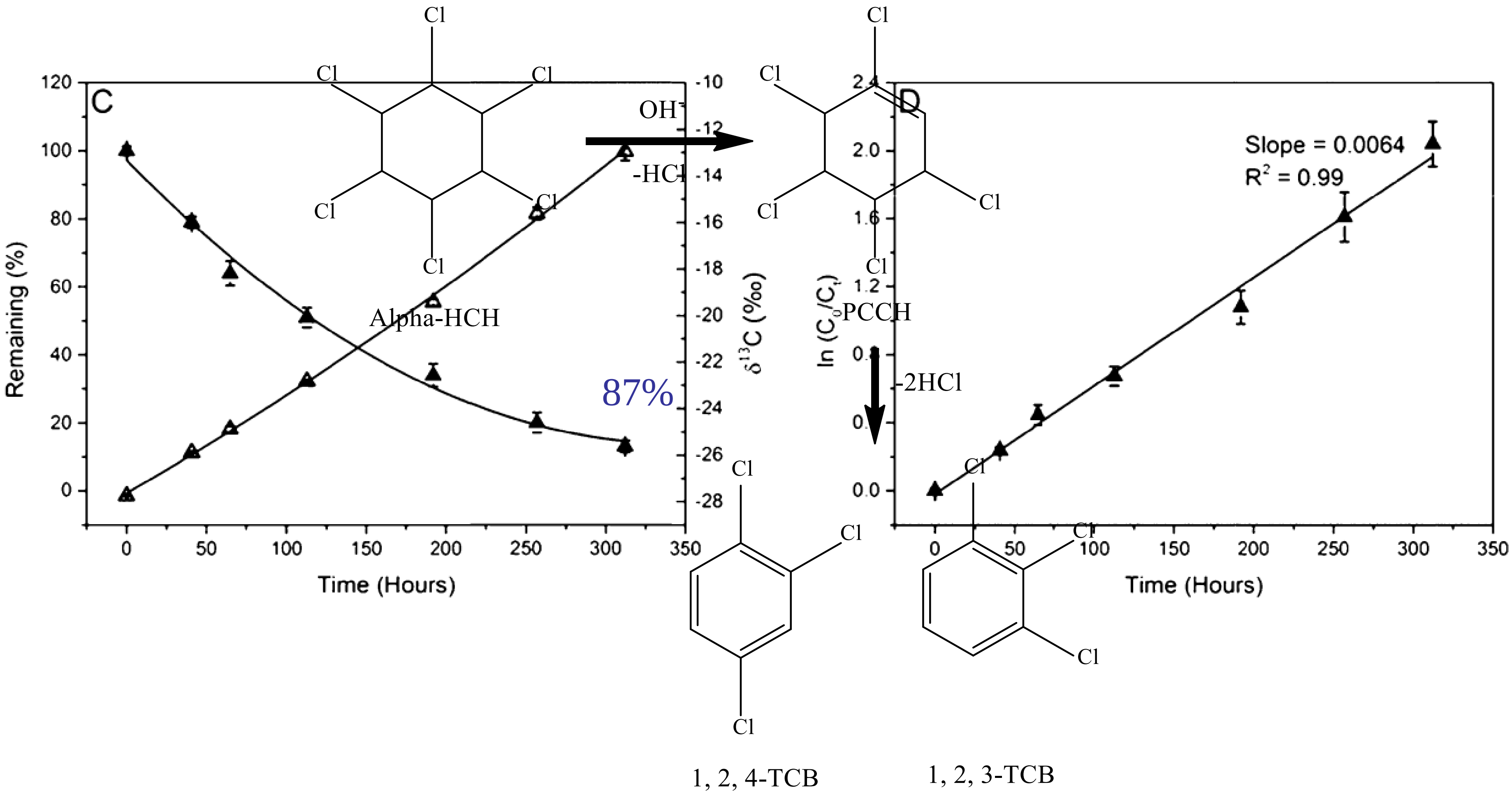
3.1. Direct and indirect photolysis

(1) Direct photolysis; (2) Indirect photolysis



Result

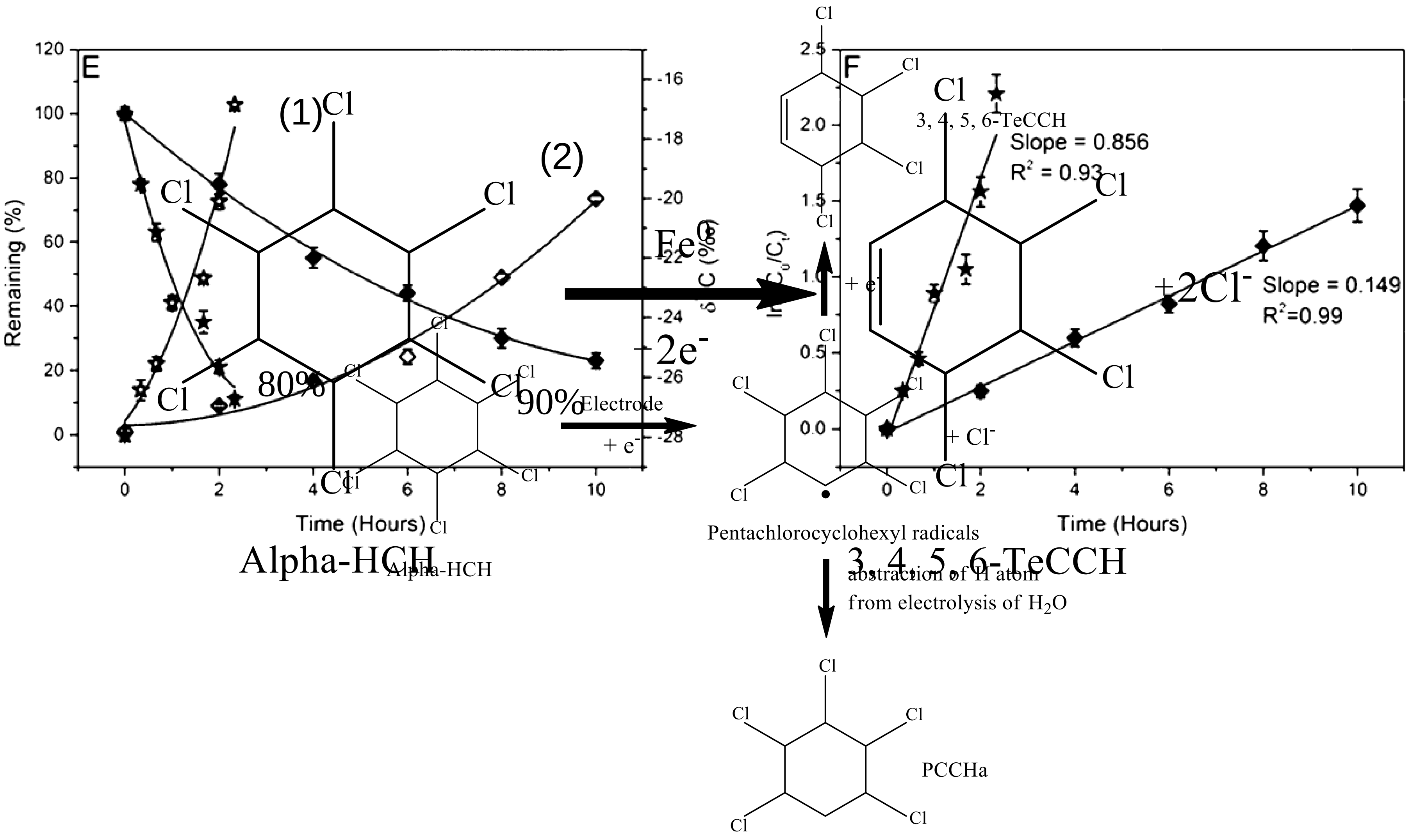
3.2. Alkaline hydrolysis



Result

3.3 Electrochemical reduction and Reduction by Fe^0 nanoparticles

(1) Electrochemical reduction (2) Reduction by Fe^0 nanoparticles



Discussion

4.1 Carbon isotope fractionation of the reaction mechanisms

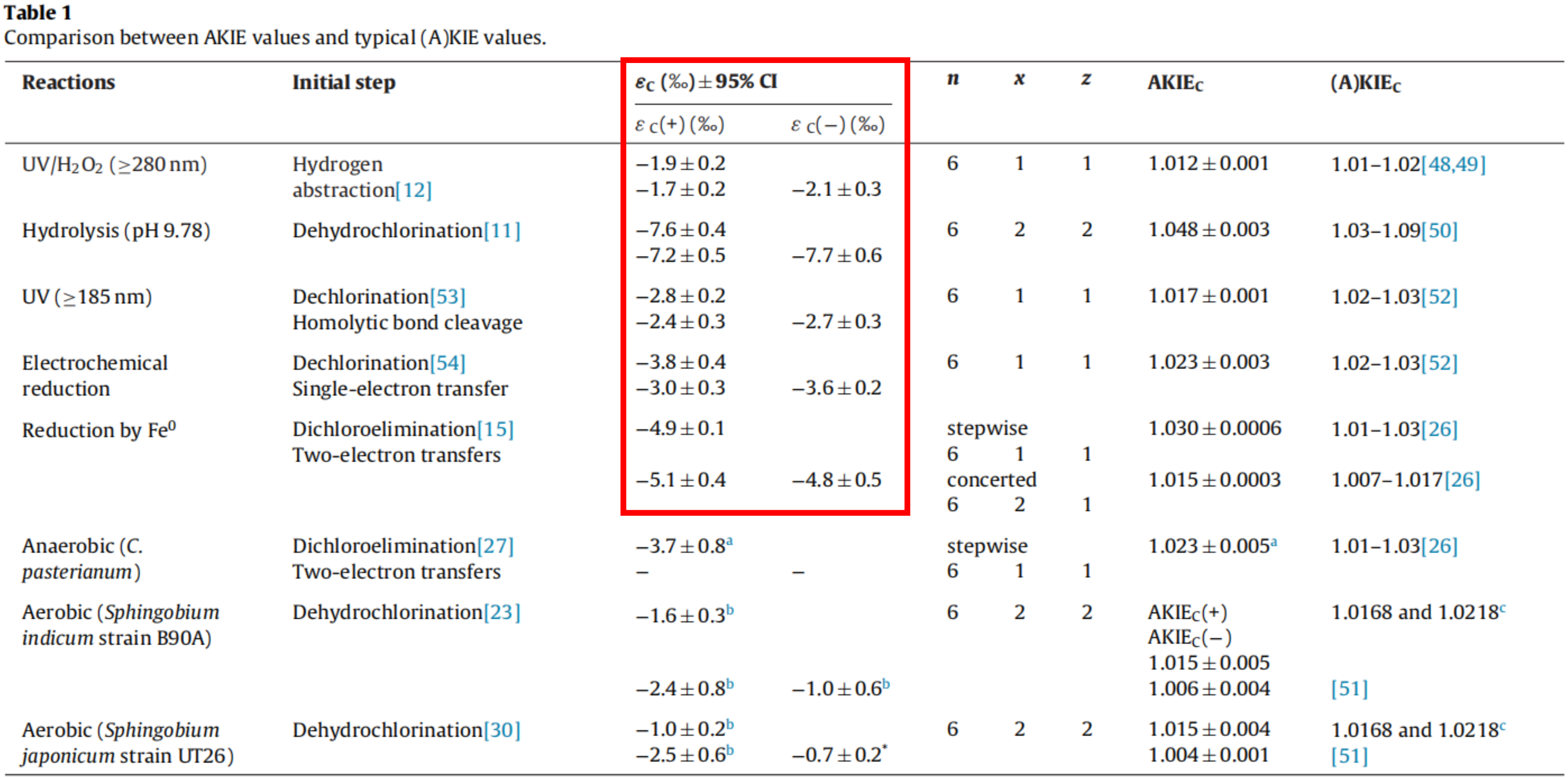


Table 1
Comparison between AKIE values and typical (A)KIE values.

Reactions	**Initial step**	**ε_C (‰) ± 95% CI**		***n***	***x***	***z***	**$\mathrm{AKIE_C}$**	**(A)$\mathrm{KIE_C}$**
		$\varepsilon_C(+)$ (‰)	$\varepsilon_C(-)$ (‰)					
UV/H_2O_2 (≥280 nm)	Hydrogen abstraction[12]	−1.9 ± 0.2 −1.7 ± 0.2	−2.1 ± 0.3	6	1	1	1.012 ± 0.001	1.01–1.02[48,49]
Hydrolysis (pH 9.78)	Dehydrochlorination[11]	−7.6 ± 0.4 −7.2 ± 0.5	−7.7 ± 0.6	6	2	2	1.048 ± 0.003	1.03–1.09[50]
UV (≥185 nm)	Dechlorination[53] Homolytic bond cleavage	−2.8 ± 0.2 −2.4 ± 0.3	−2.7 ± 0.3	6	1	1	1.017 ± 0.001	1.02–1.03[52]
Electrochemical reduction	Dechlorination[54] Single-electron transfer	−3.8 ± 0.4 −3.0 ± 0.3	−3.6 ± 0.2	6	1	1	1.023 ± 0.003	1.02–1.03[52]
Reduction by Fe^0	Dichloroelimination[15] Two-electron transfers	−4.9 ± 0.1		stepwise 6	1	1	1.030 ± 0.0006	1.01–1.03[26]
		−5.1 ± 0.4	−4.8 ± 0.5	concerted 6	2	1	1.015 ± 0.0003	1.007–1.017[26]
Anaerobic (*C. pasterianum*)	Dichloroelimination[27] Two-electron transfers	−3.7 ± 0.8[a] –	–	stepwise 6	1	1	1.023 ± 0.005[a]	1.01–1.03[26]
Aerobic (*Sphingobium indicum* strain B90A)	Dehydrochlorination[23]	−1.6 ± 0.3[b]		6	2	2	$\mathrm{AKIE_C}(+)$ $\mathrm{AKIE_C}(-)$ 1.015 ± 0.005	1.0168 and 1.0218[c]
		−2.4 ± 0.8[b]	−1.0 ± 0.6[b]				1.006 ± 0.004	[51]
Aerobic (*Sphingobium japonicum* strain UT26)	Dehydrochlorination[30]	−1.0 ± 0.2[b] −2.5 ± 0.6[b]	−0.7 ± 0.2[*]	6	2	2	1.015 ± 0.004 1.004 ± 0.001	1.0168 and 1.0218[c] [51]

Larger carbon isotope fractionations were observed for C-Cl bond cleavage reactions (direct photolysis, electro-reduction and reduction by Fe^0) compared to C-H bond cleavage by OH radical-induced oxidation (indirect photolysis).

discussion

4.2 Comparison of chemical and biological isotope fractionation

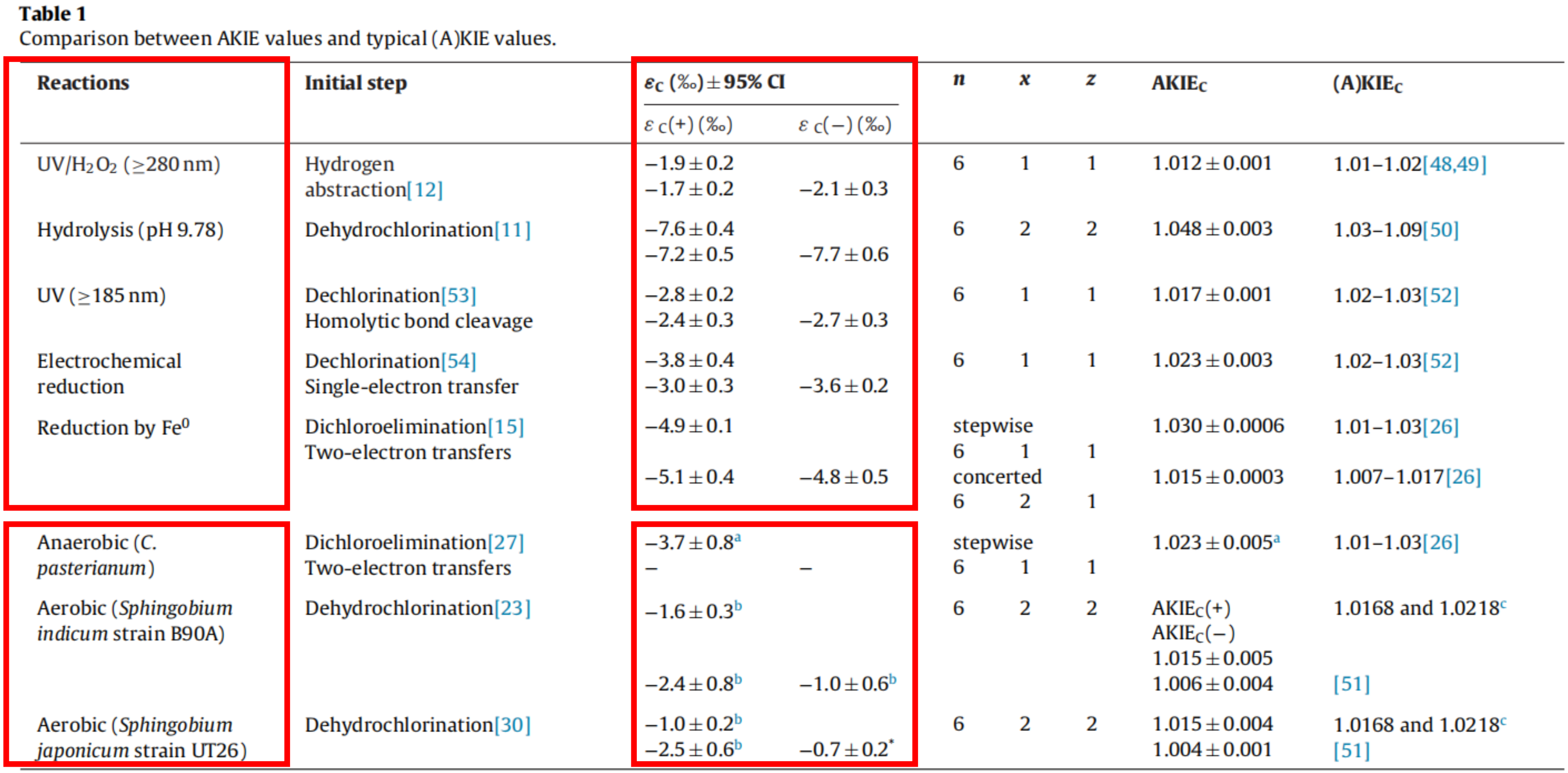


Table 1
Comparison between AKIE values and typical (A)KIE values.

Reactions	**Initial step**	ε_C (‰) ± 95% CI $\varepsilon_C(+)$ (‰)	 $\varepsilon_C(-)$ (‰)	*n*	*x*	*z*	**AKIE$_C$**	**(A)KIE$_C$**
UV/H_2O_2 (≥280 nm)	Hydrogen abstraction[12]	−1.9 ± 0.2 −1.7 ± 0.2	−2.1 ± 0.3	6	1	1	1.012 ± 0.001	1.01–1.02[48,49]
Hydrolysis (pH 9.78)	Dehydrochlorination[11]	−7.6 ± 0.4 −7.2 ± 0.5	−7.7 ± 0.6	6	2	2	1.048 ± 0.003	1.03–1.09[50]
UV (≥185 nm)	Dechlorination[53] Homolytic bond cleavage	−2.8 ± 0.2 −2.4 ± 0.3	−2.7 ± 0.3	6	1	1	1.017 ± 0.001	1.02–1.03[52]
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Reduction by Fe^0	Dichloroelimination[15] Two-electron transfers	−4.9 ± 0.1		stepwise 6	1	1	1.030 ± 0.0006	1.01–1.03[26]
		−5.1 ± 0.4	−4.8 ± 0.5	concerted 6	2	1	1.015 ± 0.0003	1.007–1.017[26]
Anaerobic (*C. pasterianum*)	Dichloroelimination[27] Two-electron transfers	−3.7 ± 0.8[a] –	 –	stepwise 6	1	1	1.023 ± 0.005[a]	1.01–1.03[26]
Aerobic (*Sphingobium indicum* strain B90A)	Dehydrochlorination[23]	−1.6 ± 0.3[b] −2.4 ± 0.8[b]	−1.0 ± 0.6[b]	6	2	2	AKIE$_C$(+) AKIE$_C$(−) 1.015 ± 0.005 1.006 ± 0.004	1.0168 and 1.0218[c] [51]
Aerobic (*Sphingobium japonicum* strain UT26)	Dehydrochlorination[30]	−1.0 ± 0.2[b] −2.5 ± 0.6[b]	−0.7 ± 0.2[*]	6	2	2	1.015 ± 0.004 1.004 ± 0.001	1.0168 and 1.0218[c] [51]

The ε_C of α-HCH for chemical transformation was systematicallyhigher compared to biological transformation, the extent of carbon isotope fractionation may allow distinguishing biological and chemical reactions.

discussion

4.3. Apparent kinetic isotope effect (AKIE)

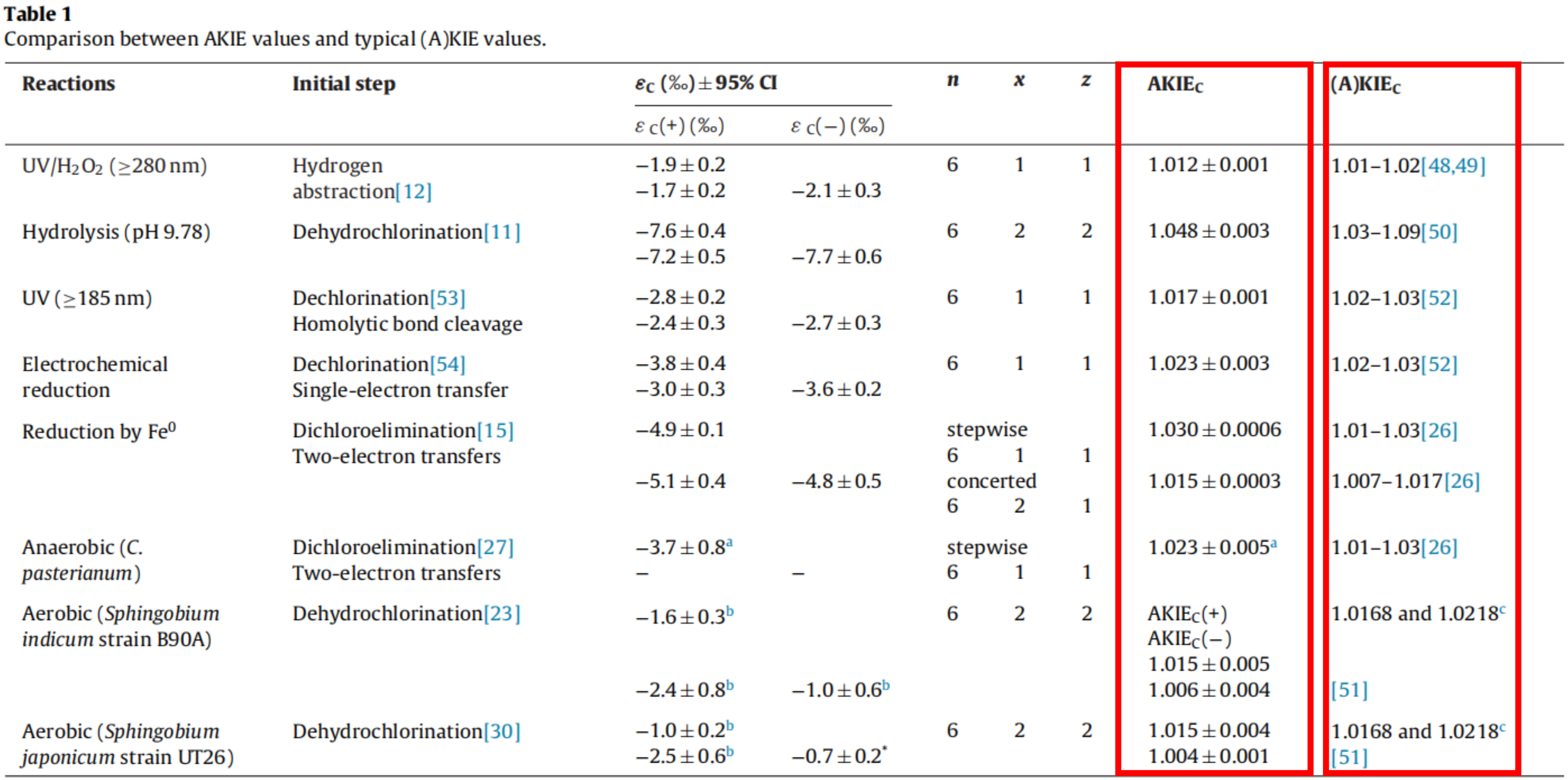

Table 1
Comparison between AKIE values and typical (A)KIE values.

Reactions	**Initial step**	ε_C (‰) ± 95% CI		***n***	***x***	***z***	**AKIE$_C$**	**(A)KIE$_C$**
		$\varepsilon_C(+)$ (‰)	$\varepsilon_C(-)$ (‰)					
UV/H_2O_2 (≥280 nm)	Hydrogen abstraction[12]	−1.9 ± 0.2		6	1	1	1.012 ± 0.001	1.01–1.02[48,49]
		−1.7 ± 0.2	−2.1 ± 0.3					
Hydrolysis (pH 9.78)	Dehydrochlorination[11]	−7.6 ± 0.4		6	2	2	1.048 ± 0.003	1.03–1.09[50]
		−7.2 ± 0.5	−7.7 ± 0.6					
UV (≥185 nm)	Dechlorination[53] Homolytic bond cleavage	−2.8 ± 0.2		6	1	1	1.017 ± 0.001	1.02–1.03[52]
		−2.4 ± 0.3	−2.7 ± 0.3					
Electrochemical reduction	Dechlorination[54] Single-electron transfer	−3.8 ± 0.4		6	1	1	1.023 ± 0.003	1.02–1.03[52]
		−3.0 ± 0.3	−3.6 ± 0.2					
Reduction by Fe^0	Dichloroelimination[15] Two-electron transfers	−4.9 ± 0.1		stepwise 6	1	1	1.030 ± 0.0006	1.01–1.03[26]
		−5.1 ± 0.4	−4.8 ± 0.5	concerted 6	2	1	1.015 ± 0.0003	1.007–1.017[26]
Anaerobic (*C. pasterianum*)	Dichloroelimination[27] Two-electron transfers	−3.7 ± 0.8[a]		stepwise 6	1	1	1.023 ± 0.005[a]	1.01–1.03[26]
		–	–					
Aerobic (*Sphingobium indicum* strain B90A)	Dehydrochlorination[23]	−1.6 ± 0.3[b]		6	2	2	AKIE$_C$(+) AKIE$_C$(−)	1.0168 and 1.0218[c]
		−2.4 ± 0.8[b]	−1.0 ± 0.6[b]				1.015 ± 0.005 1.006 ± 0.004	[51]
Aerobic (*Sphingobium japonicum* strain UT26)	Dehydrochlorination[30]	−1.0 ± 0.2[b]		6	2	2	1.015 ± 0.004	1.0168 and 1.0218[c]
		−2.5 ± 0.6[b]	−0.7 ± 0.2[*]				1.004 ± 0.001	[51]

The calculation of apparent kinetic isotope effect (AKIE) allows comparing isotope effects of bond changes which can be used to gain insight into the chemical reaction mechanisms.

discussion

4.4. Enantiomeric fraction and isotope discrimination

- ESIA approach is suitable to differentiate between chemical transformation and aerobic biodegradation.

- However, the range of chemical transformation partially overlaps with those of anaerobic biodegradation, thus, the distinction of these transformation processes seems to be not always possible.

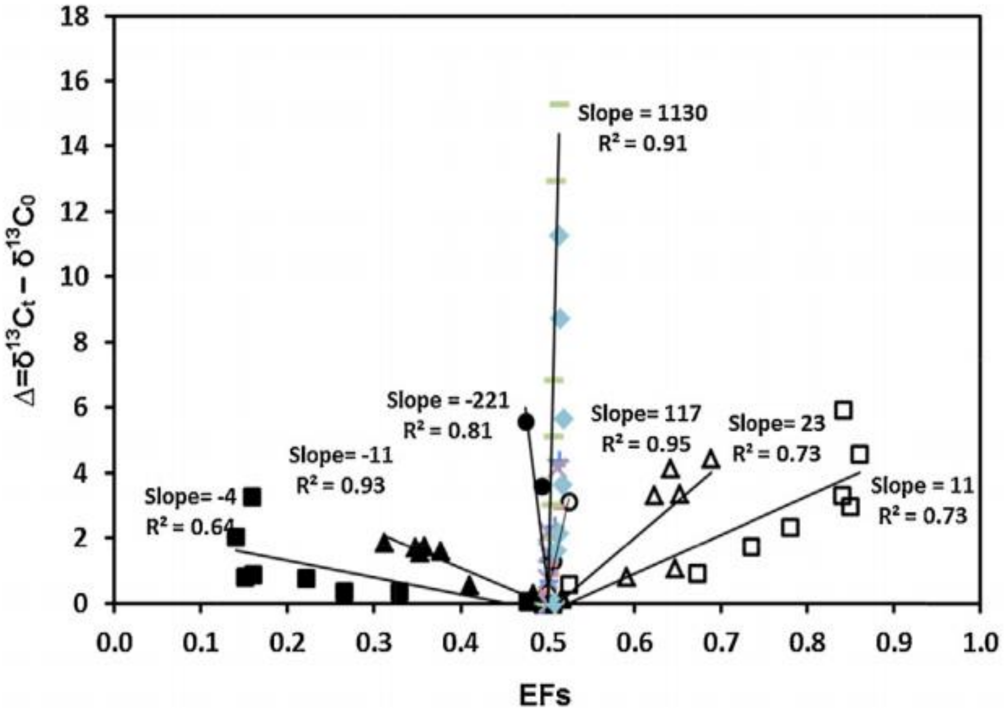

Fig. Comparison of carbon isotope discrimination ($\delta^{13}C_t - \delta^{13}C_0$) vs enantiomeric fraction (EF) for (+) α-HCH (EF (+)) (open symbols) and (−) α-HCH (EF (−)) (closed symbols)for anaerobic biodegradationby Clostridium pasterianum (circles) andaerobic biodegradation by Sphingobium indicum strain B90A (squares) and Sphingobium japonicum strain UT26 (triangles). Cdirect photolysis (+), indirect photolysis (—), hydrolysis (—), electrochemical reduction (×) and reduction by Fe0 (◆). The slope is only shown for hydrolysis due to the overlap with other chemical reactions.

Conclusion

- The stable carbon isotope fractionation for the different reaction mechanisms obtained in our study can, thereby, be used as references for evaluating field data in order to determine the relevance of chemical and biological α-HCH transformation in the environment.
- Our study demonstrates that CSIA in combination with ESIA and the determination of EF value is feasible as a generic concept for characterizing the transformation of chiral contaminants. But, due to the low enantioselectivity for both chemical transformation and anaerobic biodegradation of α-HCH, the applicability to distinguish these reactions is limited.
- It should be possible to apply the multi-element CSIA for a better characterization of transformation pathways, e.g., between C-H and C-Cl bond cleavage involved reactions.
- Overall, these approaches will provide new perspectives for detailedevaluation of the fate of α-HCH.

Thanks for your attention!