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基于 Gaussian、ECOSAR 模型的紫外/次氯酸体系降解含卤阻燃剂的产物预测与毒性评估*

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摘 要 含卤阻燃剂广泛应用于各类电子产品的生产, 难降解且具有生物毒性. 在生产和使用过程中, 部分含卤阻燃剂会残留在水体并排放到水环境造成累积污染, 威胁水环境安全, 亟需探寻有效的降解去毒方法. 本研究通过 Gaussian 与 ECOSAR 模型预测了四氯双酚 A (TCBPA)、四溴双酚 A (TBBPA)、十溴二苯乙烷 (DBDPE) 等 3 种典型含卤阻燃剂在紫外/次氯酸 (UV/Cl) 体系中的光催化降解路径与产物毒性. 结果表明, UV/Cl 体系中的含氯自由基 (RCS) 与羟基自由基 ($\cdot\text{OH}$) 易攻击阻燃剂分子结构上键能较低、Fukui 指数较高的位点, 促使 C—Cl 键、C—Br 键、C—C 键等因为受到攻击而断裂, 进而降解阻燃剂. 同时, 利用 ECOSAR 模型评估发现降解产物的急性毒性 $\text{LC}_{50-96\text{ h}}$ 均低于 $100\text{ mg}\cdot\text{L}^{-1}$, 佐证了 UV/Cl 体系对含卤阻燃剂降解的有效性, 并降低其环境危害. 因此, 采用 Gaussian 计算、ECOSAR 模型相结合的分析方法, 能够更加便捷地预测阻燃剂降解路径与产物毒性特征, 为深入揭示 UV/Cl 体系光催化降解含卤阻燃剂机理提供新思路.

关键词 Gaussian, Fukui 指数, ECOSAR 模型, 含卤阻燃剂, 紫外/次氯酸, 生物毒性.

Product prediction and toxicity assessment of halogen-containing flame retardants degraded by UV/hypochlorous acid systems based on Gaussian and ECOSAR models

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Abstract Halogen-containing flame retardants are extensively used in the production of various electronic products, which will inevitably be discharged into surface water, causing cumulative pollution, and threatening the safety of the aquatic environment for their persistent stability and biological toxicity. Thus, it is urgent to explore effective degradation and detoxification methods. In

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this study, the Gaussian and ECOSAR models were employed to predict the performance of three typical halogen-containing flame retardants including TCBPA (tetrachlorobisphenol A), TBBPA (tetrabromobisphenol A), and DBDPE (decabromodiphenylethane) in ultraviolet excited hypochlorous acid (UV/Cl) systems for evaluating their photocatalytic oxidation degradation pathways and products toxicity. The results showed that the chlorine-containing radicals (RCS) and hydroxyl radicals ($\cdot\text{OH}$) in the UV/Cl system were prone to attack the sites with lower bond energy and higher Fukui index on the molecular structure of the flame retardant, which promoted the degradation of flame retardants through the cleavage of C—Cl Bonds, C—Br bonds, C—C bonds, etc. Meanwhile, the ECOSAR model was used to evaluate the acute toxicity $\text{LC}_{50-96\text{ h}}$ of the degradation products, which were all lower than $100\text{ mg}\cdot\text{L}^{-1}$, and proved the effectiveness of halogen-containing flame retardants in the UV/Cl process and reduced their environmental hazards. Therefore, the combined analysis method of Gaussian calculation and ECOSAR model conveniently predicted the degradation path and product toxicity characteristics of flame retardants, and provided new insights into further revealing the mechanism of photocatalytic oxidation degradation of halogen-containing flame retardants in UV/Cl system.

Keywords Gaussian, Fukui index, ECOSAR, halogen-containing flame retardants, ultraviolet/hypochlorous acid, biological toxicity.

含卤阻燃剂是一类能阻止聚合物材料引燃或抑制火焰传播的含卤有机化合物,包括“氯系阻燃剂”和“溴系阻燃剂”,由于其阻燃效果好,添加量少,性能优异,广泛应用于各类电子产品的生产过程中^[1].在工业生产及日常使用过程中,一些含卤阻燃剂被废弃后会在环境中残留^[2].相关研究表明,四氯双酚 A (TCBPA) 在河流沉积样中被检测出浓度达到 $542.6\text{ ng}\cdot\text{g}^{-1}$; 四溴双酚 A (TBBPA) 在废水中浓度为 $10^2\text{—}10^3\text{ ng}\cdot\text{L}^{-1}$, 十溴二苯乙烷 (DBDPE) 在制造工厂土壤中浓度最高达 $34000\text{ ng}\cdot\text{g}^{-1}$ ^[3-5].部分含卤阻燃剂由于具有持久性、生物富集毒性和长距离迁移等特性,经过在环境中的长期累积^[6-9],成为威胁环境安全的污染物,对生物和人类的健康造成不良影响^[10-13].因此,对含卤阻燃剂进行降解减毒研究具有重要意义.

目前,对含卤阻燃剂的降解方法主要有微生物降解、高温热处理、高级氧化等技术.微生物降解技术虽然成本较低,但降解缓慢,降解周期长;高温热处理技术通过使污染物在高温下氧化热解作用而达降解,该方法过程简单、降解效率高,但在高温环境降解过程中可能产生有毒气体和其它有毒副产物,造成二次污染;高级氧化技术具有反应速度快,降解效率高,氧化能力强等优点,是近年来较被广泛关注的阻燃剂降解工艺^[14-17].相较于上述工艺,紫外/次氯酸 (UV/Cl) 体系能够为饮用水处理系统提供多种消毒屏障^[18],体系中的余氯具有持续的消毒作用,是新兴的高级氧化工艺,它常用作自来水厂、污水处理厂中水体的消毒.该体系通过产生高活性的含氯自由基 (RCS)^[19-20],对污染物的富电子基团进行攻击,从而实现了对污染物的降解,但降解后的产物种类和产物的毒性鉴定需要高端昂贵仪器或复杂实验检测分析^[21-22],一般实验室研究人员无法企及.该研究采用 Gaussian 模型和 Multiwfn 程序通过非实验测试的方法计算出有机物分子中各化学键的键能和 Fukui 指数,判断各活性位点的化学属性,从而实现降解产物的推测. ECOSAR 能够通过定量构效关系 (QSAR) 来对有机物的毒性进行预测^[23],但采用 Gaussian 计算、ECOSAR 模型对阻燃剂的降解路径和毒性预测仍鲜见研究报道.

该研究选择模拟 UV/Cl 的高级氧化工艺,对 TCBPA、TBBPA、DBDPE 这 3 种代表性的含卤阻燃剂的降解产物进行预测与毒性评估.采用 Gaussian 软件与 Multiwfn 程序对 TCBPA、TBBPA、DBDPE 上位点的键能及 Fukui 指数进行计算,从而预测出降解产物路径,并用 ECOSAR 软件对预测出的降解产物进行毒性评估,旨在为难降解毒害性有机物光催化降解路径、机理与产物毒性特征的预测分析提供新思路.

1 材料与方法(Materials and methods)

1.1 键能的计算

通过 GaussView5.0 构建含卤阻燃剂各组分结构后,选择几何优化与振动频率分析(Opt+Freq),以密度泛函理论(DFT)为基础,使用 B3LYP 方法,基组水平设置为 6-31G(2df, 2p),设置 100 MB 的计算储存空间用于保存 input 文件,并将 input 文件在 Gaussian 09W 软件中打开,将循环次数(maxcycle)设置为 200,以确保计算结果的准确性. Gaussian 09W 计算完成后,将含卤阻燃剂各组分结构的 out 文件中的结果参照公式(1)进行计算,将化学键断裂后两个离解部分的分子能量之和扣除初始化合物的分子能量,即为化学键离解能^[24].

$$D_3 = D_1 + D_2 - D \quad (1)$$

式中 D_1 、 D_2 分别表示两个离解部分的分子能量, D_3 表示键离解能, D 表示初始化合物的分子能量.

1.2 Fukui 指数的计算

基于密度函数理论(DFT)通过 Multiwfn 程序计算上述含卤阻燃剂的 Fukui 指数. Fukui 指数是由于分子中的电子数的变化而引起的分子中的电子密度函数变化^[25-27],它能够提供分子得到或失去电子的电势信息,从而通过数值的高低预测分子中更易受到亲电(f^-)或者亲核攻击(f^+)的位点^[28].

1.3 采用 ECOSAR 模型对降解产物毒性的预测

QSAR 模型能够将化学活性与分子结构和组成相联系,从而预测有机物毒性^[29]. 研究表明, ECOSAR 软件被认为是估计水生毒性的最佳效果预测程序之一,并且通过将 ECOSAR 软件的预测值与实测值进行比较,证实了 ECOSAR 软件的可靠性及有效性^[30-35]. 因此采用 ECOSAR Version 2.0 (2000-2016 U.S. Environmental Protection Agency)软件能够预测含卤阻燃剂降解产物对鱼类的毒性,通过毒性数据判断所预测的阻燃剂及其降解产物的生态危害水平.

2 结果与讨论(Results and discussion)

2.1 阻燃剂各组分键能分析

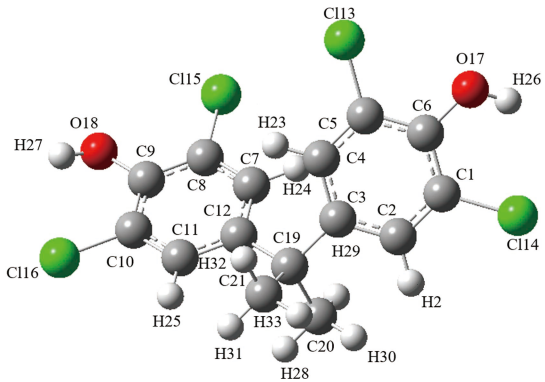
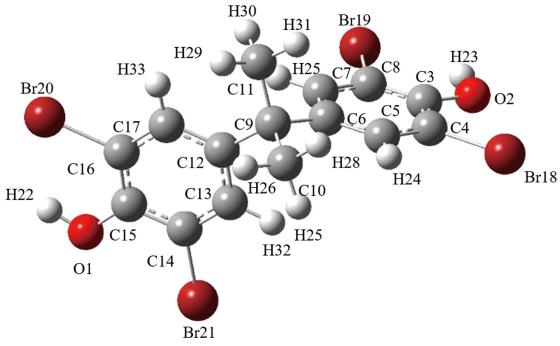
Gaussian 09 对阻燃剂各位点键能的计算结果如表 1 所示,可以发现在 TCBPA 结构中,键 C5—C113、C8—C115 的键能最小,均为 256.0496 kJ·mol⁻¹,键能较接近的还有键 C1—C114、C10—C116,它们的键能均为 261.7385 kJ·mol⁻¹,这 4 个键的键能较其他位点低,更容易受到自由基的攻击而产生取代、加成等反应. 在 TBBPA 结构中, C9—C10、C9—C11 是结构中键能最小的两个键,且两个键的键能接近,分别为 272.2355 kJ·mol⁻¹、272.6038 kJ·mol⁻¹,因此这两个键断裂所需的能量相较于其他键最小,较容易断裂. 在 DBDPE 结构中,最小键能的 C1—C2 仅为 258.8407 kJ·mol⁻¹,相比之下更容易断裂,在 UV/Cl 体系中受到 RCS (活性氯自由基)、·OH 等自由基的攻击的可能性最大.

2.2 Fukui 指数分析预测化学键断裂位点

Fukui 指数中 f^- 的数值能够表征活性位点受到自由基攻击的难易程度, f^- 的数值越大表明越容易受到氧化性自由基的攻击^[36]. 因此,该研究通过引入 Fukui 指数,对键能预测断键点位的准确性加以佐证. 通过分析表 2 可以发现,在 TBBPA 结构中,位点 Br18($f^- = 0.1164$)、Br20($f^- = 0.0889$)、Br21($f^- = 0.0814$)的 f^- 指数最高,与结构中键能低的位点基本吻合. 在 TCBPA 结构(表 3)中,位点 C113($f^- = 0.0685$)、C114($f^- = 0.0765$)、C115($f^- = 0.0685$)、C116($f^- = 0.0765$)的 f^- 指数相对较高,因此,在 UV/Cl 体系中,上述四位点最容易受到 RCS 与 ·OH 的攻击,与表 1 键能计算所预测的位点基本一致. 在 DBDPE 结构(表 4)中,具有最高的 f^- 指数的位点为 Br9($f^- = 0.0909$)、Br10($f^- = 0.0841$)、Br12($f^- = 0.1009$)、Br21($f^- = 0.1009$)、Br23($f^- = 0.0841$)、Br24($f^- = 0.0908$),与 Gaussian 计算出的 DBDPE 结构中的键能较低的位点相吻合,推测在降解过程中更容易产生断裂.

表 1 各阻燃剂不同点位键能分布

Table 1 Different point bond energy distribution of each flame retardant

	位点 Sites	键能/(kJ·mol ⁻¹) Bond energy
	5C-13Cl	256.0496
	8C-15Cl	256.0496
	1C-14Cl	261.7385
	10C-16Cl	261.7385
	19C-21C	273.4115
	19C-20C	273.4115
	3C-19C	329.8949
	12C-19C	329.8952
	17O-26H	364.9065
	18O-27H	364.9082
	20C-30H	450.0166
	20C-28H	450.0167
	21C-33H	450.0167
	21C-31H	450.0168
	20C-29H	450.0169
	21C-32H	450.0169
	6C-17O	454.1277
	2C-22H	496.3993
	11C-25H	496.3993
	4C-23H	500.8255
7C-24H	500.9393	
9C-18O	527.4504	
	9C-11C	272.2355
	9C-10C	272.6038
	9C-12C	331.2436
	6C-9C	331.2438
	14C-21Br	343.9736
	4C-18Br	345.0387
	8C-19Br	351.9484
	16C-20Br	352.7075
	10-22H	366.4833
	20-23H	366.8199
	11C-29H	449.7797
	11C-30H	449.7797
	11C-31H	449.7797
	10C-26H	449.9446
	10C-27H	449.9446
	10C-28H	449.9446
	15C-10	461.6979
	3C-20	461.9418
17C-33H	494.5618	
5C-24H	495.2022	
7C-25H	498.5851	
13C-32H	499.4345	

续表 1

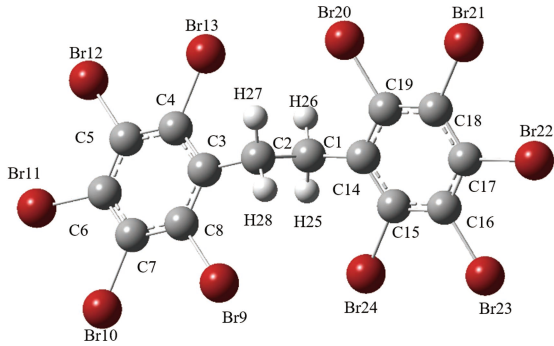
	位点 Sites	键能/(kJ·mol ⁻¹) Bond energy
	1C-2C	258.8407
	6C-11Br	318.5690
	17C-22Br	318.5690
	7C-10Br	320.1635
	16C-23Br	320.1635
	5C-12Br	321.4881
	18C-21Br	321.4881
	4C-13Br	321.5290
	19C-20Br	321.5290
	8C-9Br	322.8489
	15C-24Br	322.8489
	1C-25H	407.1854
	2C-27H	407.1854
	2C-28H	407.1854
	1C-26H	407.1857
	1C-14C	433.1090
	2C-3C	433.1090

表 2 四溴双酚 A 不同点位 Fukui 指数

Table 2 Fukui index at different points of tetrabromobisphenol A

原子 Atom	序号 Serial number	$q_{(N)}$	$q_{(N+1)}$	$q_{(N-1)}$	f^-	f^+
Br	18	-0.0369	-0.1557	0.0795	0.1164	0.1188
Br	20	-0.0259	-0.1863	0.063	0.0889	0.1604
Br	21	-0.0338	-0.1413	0.0476	0.0814	0.1075
Br	19	-0.0224	-0.1674	0.0479	0.0703	0.145
O	1	-0.1869	-0.2114	-0.1251	0.0618	0.0246
O	2	-0.1872	-0.2116	-0.1254	0.0618	0.0244
C	3	0.0682	0.0499	0.1125	0.0442	0.0183
C	15	0.0682	0.0493	0.1119	0.0437	0.019
C	6	0.0004	-0.0094	0.0379	0.0375	0.0098
C	12	0.0006	-0.0096	0.0374	0.0367	0.0102
C	4	-0.0079	-0.0364	0.0246	0.0325	0.0285
C	16	-0.0147	-0.054	0.0127	0.0274	0.0392
C	7	-0.0447	-0.065	-0.0179	0.0268	0.0203
C	17	-0.0489	-0.0692	-0.026	0.023	0.0202
C	14	-0.0055	-0.0297	0.0124	0.0179	0.0242
C	5	-0.0457	-0.067	-0.0287	0.017	0.0213
C	13	-0.0417	-0.065	-0.026	0.0157	0.0233
C	8	-0.0115	-0.0451	0.0039	0.0154	0.0336
C	10	-0.0826	-0.0885	-0.0728	0.0098	0.0059
C	11	-0.0833	-0.0887	-0.0735	0.0097	0.0054
C	9	0.0304	0.0271	0.0333	0.0029	0.0033

表 3 四氯双酚 A 不同点位 Fukui 指数

Table 3 Fukui index at different points of tetrachlorobisphenol A

原子 Atom	序号 Serial number	$q(N)$	$q(N+1)$	$q(N-1)$	f^-	f^+
Cl	14	-0.0648	-0.2085	0.0118	0.0765	0.1437
Cl	16	-0.0648	-0.2084	0.0118	0.0765	0.1436
Cl	13	-0.0652	-0.1624	0.0033	0.0685	0.0972
Cl	15	-0.0652	-0.1623	0.0033	0.0685	0.0971
O	18	-0.1842	-0.2135	-0.1166	0.0676	0.0294
O	17	-0.1842	-0.2135	-0.1166	0.0676	0.0293
C	9	0.0695	0.0423	0.1167	0.0472	0.0273
C	6	0.0695	0.0423	0.1167	0.0472	0.0272
C	3	0.0015	-0.0144	0.0426	0.0411	0.0159
C	12	0.0015	-0.0145	0.0426	0.0411	0.0159
C	1	0.0086	-0.0291	0.0407	0.0321	0.0377
C	10	0.0086	-0.0291	0.0407	0.0321	0.0377
C	2	-0.0481	-0.072	-0.0222	0.026	0.0239
C	11	-0.0481	-0.0719	-0.0222	0.026	0.0238
C	5	0.0195	-0.0063	0.0413	0.0219	0.0258
C	8	0.0195	-0.0063	0.0413	0.0219	0.0258
C	7	-0.0421	-0.0598	-0.0225	0.0195	0.0177
C	4	-0.0421	-0.0597	-0.0226	0.0195	0.0176
C	20	-0.0828	-0.0884	-0.0723	0.0106	0.0055
C	21	-0.0828	-0.0884	-0.0723	0.0106	0.0055
C	19	0.0306	0.026	0.0339	0.0033	0.0046

表 4 十溴二苯乙烷不同点位 Fukui 指数

Table 4 Fukui index of decabromodiphenylethane at different points

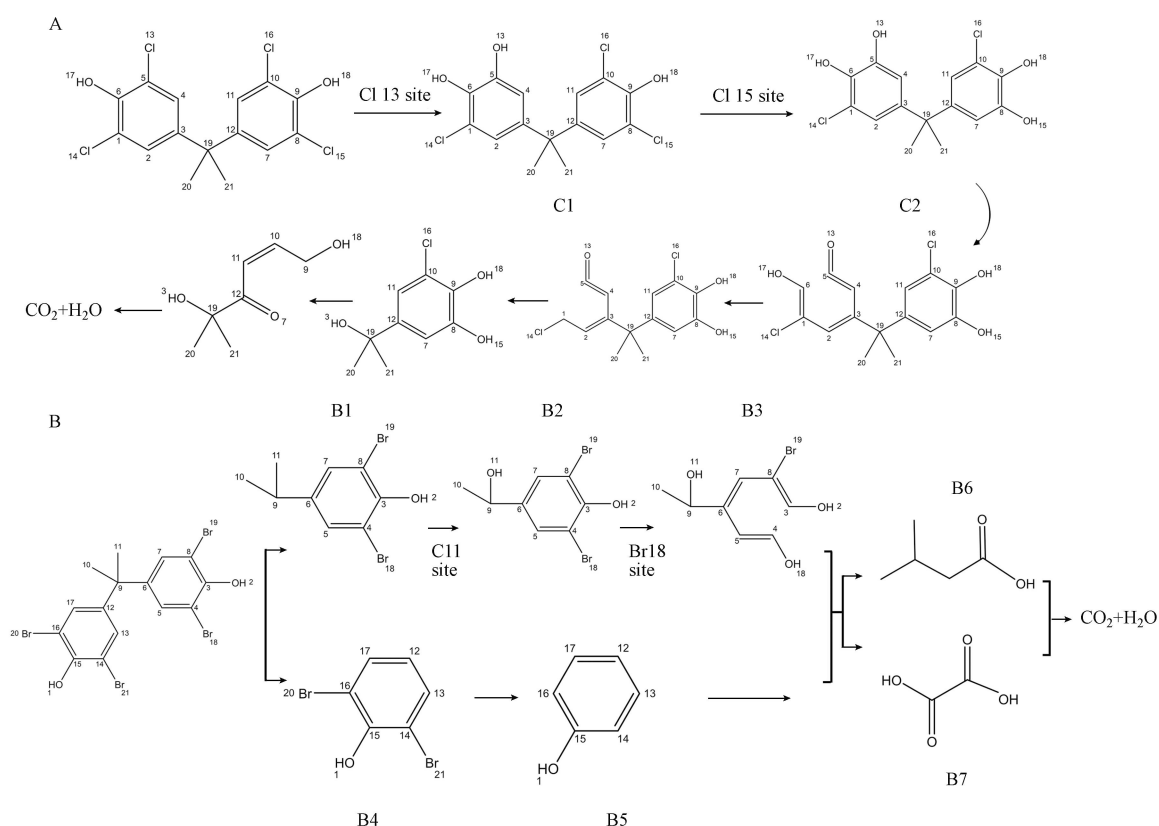
原子 Atom	序号 Serial number	$q(N)$	$q(N+1)$	$q(N-1)$	f^-	f^+
Br	12	-0.0037	-0.0893	0.0972	0.1009	0.0856
Br	21	-0.0037	-0.0893	0.0972	0.1009	0.0856
Br	9	0.0079	-0.0547	0.0987	0.0909	0.0626
Br	24	0.0079	-0.0547	0.0987	0.0908	0.0626
Br	10	-0.0042	-0.0874	0.0798	0.0841	0.0831
Br	23	-0.0042	-0.0874	0.0799	0.0841	0.0831
Br	13	0.0122	-0.0545	0.0741	0.0619	0.0667
Br	20	0.0122	-0.0545	0.0741	0.0619	0.0666
Br	11	-0.0016	-0.1035	0.0537	0.0554	0.1018
Br	22	-0.0016	-0.1035	0.0537	0.0554	0.1018
C	5	-0.0054	-0.0219	0.0204	0.0258	0.0165
C	18	-0.0054	-0.0219	0.0204	0.0258	0.0165
C	8	0.004	-0.0086	0.0265	0.0225	0.0127
C	15	0.004	-0.0086	0.0265	0.0225	0.0127
C	7	-0.0052	-0.0212	0.0131	0.0184	0.016

续表 4

原子 Atom	序号 Serial number	$q(N)$	$q(N+1)$	$q(N-1)$	f^-	f^+
C	16	-0.0052	-0.0212	0.0131	0.0184	0.016
C	4	0.0037	-0.0099	0.0219	0.0182	0.0136
C	19	0.0037	-0.0099	0.0219	0.0182	0.0136
C	6	-0.0037	-0.022	0.0036	0.0072	0.0183
C	17	-0.0037	-0.022	0.0036	0.0072	0.0183
C	3	0.0059	-0.0017	0.0109	0.0049	0.0076
C	14	0.0059	-0.0017	0.0108	0.0049	0.0076
C	1	-0.056	-0.0611	-0.0541	0.0019	0.0051
C	2	-0.056	-0.0611	-0.0542	0.0019	0.0051

2.3 模拟 UV/Cl 体系下的降解产物路径预测

在 UV/Cl 体系中, RCS 与 $\cdot\text{OH}$ 对 TCBPA 的降解起主导作用, 由于键 C5—Cl13、C8—Cl15 的键能最低, RCS 与 $\cdot\text{OH}$ 首先攻击这两个位点, 位点随之被 $\cdot\text{OH}$ 取代, 随着反应的进一步进行, TCBPA 上的键进一步断裂, 降解路径如图 1(A) 所示, 预测的最终产物与 Wan 等^[37] 的实验研究所得一致. TBBPA 结构中, 键 C9—C11 的键能最小, 因此在 UV/Cl 体系中的 RCS 与 $\cdot\text{OH}$ 使其断裂为 B1、B4 两部分, B4 通过 $\cdot\text{OH}$ 的氧化作用产生脱溴从而进一步转化为苯酚, B1 的降解路径如图 1(B) 所示. 经研究, 预测产物与 Guo 等^[38] 实验研究结论基本一致, 再次验证了反应体系中的 RCS 和 $\cdot\text{OH}$ 会对键能较低, 即活性较高的位点进行攻击. 反应体系中 RCS 与 $\cdot\text{OH}$ 对活性较高的 C1—C2 进行攻击, 由于二者的强氧化性, 使 DBDPE 在降解过程中产生一系列电子转移、脱氢与脱溴反应, 如图 1(C) 所示. 预测降解产物与 Chen 等^[39-40] 实验研究的最终降解产物相一致. 因此, 具有较低键能与较高 f -指数的位点活性更高, 自由基对这一类位点的反应性更高, 更容易对其进行攻击.



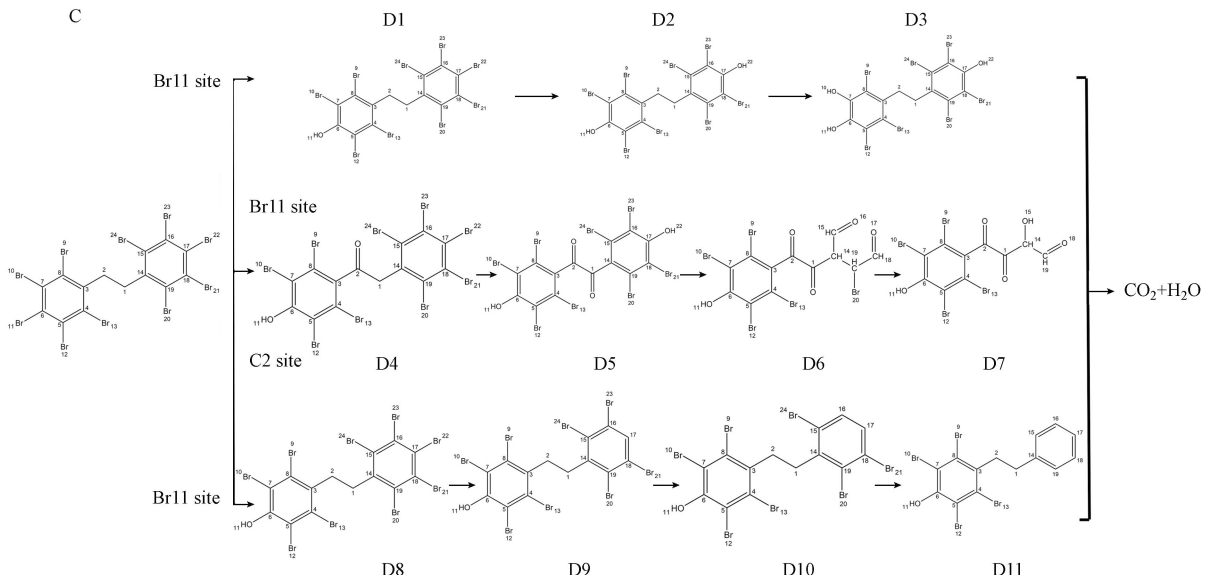


图 1 UV/Cl 体系下四氯双酚 A(TCBPA)(A)、四溴双酚 A(TBBPA)(B)和十溴二苯乙烷 (DBDPE)(C)降解路径分析
Fig.1 Degradation path analysis of TCBPA(A), TBBPA(B) and DBDPE(C) under UV/Cl system

2.4 各阻燃剂预测降解产物的毒性分析

该研究采用 ECOSAR 软件对模拟出的各阻燃剂的降解产物进行了毒性推测与分析(图 2),可以看出鱼类在 TCBPA 的溶液中 96 h 后的 LC_{50} 为 $0.06 \text{ mg}\cdot\text{L}^{-1}$, 具有非常强的毒性, 然而通过 UV/Cl 体系中自由基氧化的作用下, TCBPA 降解产物的毒性相较于 TCBPA 本身明显下降, 尤其是产物 C6 的 LC_{50} 为 $4230 \text{ mg}\cdot\text{L}^{-1}$. 如图 2(B)所示, 鱼类在 TBBPA 溶液中 96 h 后的 LC_{50} 也达 $0.023 \text{ mg}\cdot\text{L}^{-1}$, 显示 TBBPA 的降解产物毒性随着降解的逐步进行, 也出现了显著的降低, 产物 B3、B6、B7 的 LC_{50} 分别为 3.28×10^2 、 2.43×10^3 、 $1.68 \times 10^5 \text{ mg}\cdot\text{L}^{-1}$, 都达到了无害水平.

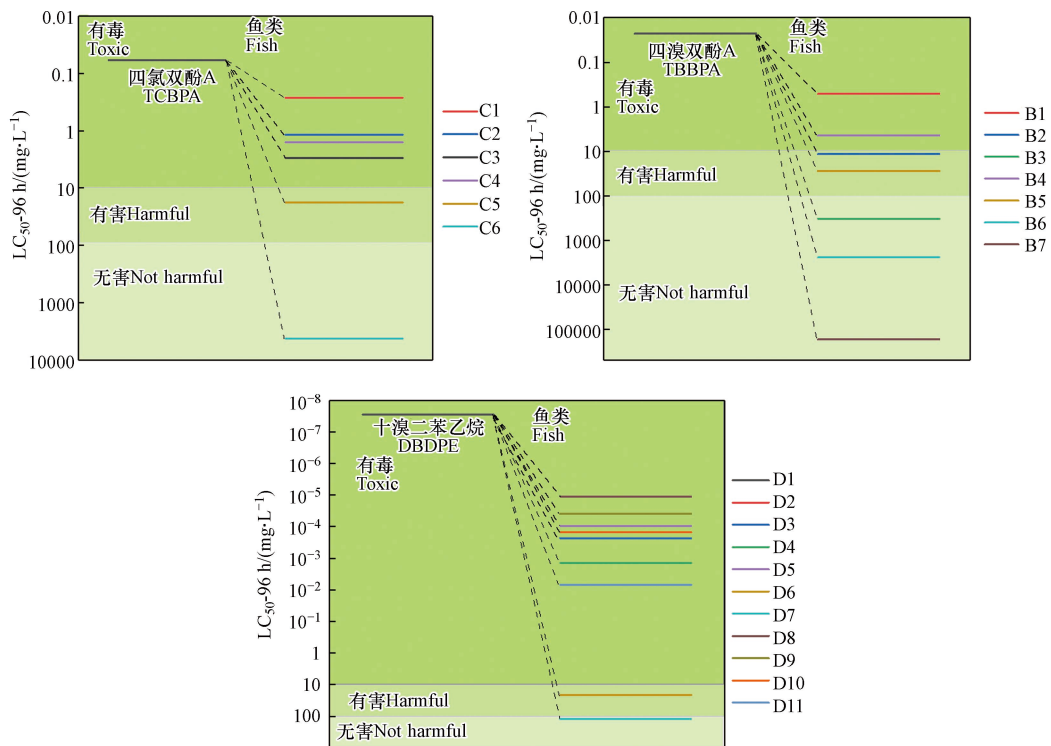


图 2 四氯双酚 A(TCBPA)(A)、四溴双酚 A(TBBPA)(B)和十溴二苯乙烷 (DBDPE)(C)在 UV/Cl 体系下降解产物的毒性
Fig.2 TCBPA(A), TBBPA(B) and DBDPE(C) reduce the toxicity of the depolyte in UV/Cl systems

在图 2(C)中,对于 DBDPE 来说,鱼类在其溶液中 96 h 的 LC_{50} 为 $2.8 \times 10^{-8} \text{ mg} \cdot \text{L}^{-1}$,毒性明显大于 TCBPA 与 TBPA,但最终通过 UV/CI 体系高效的降解, DBDPE 降解产物的毒性也逐步降低, D11 的 LC_{50} 也达到了 $124 \text{ mg} \cdot \text{L}^{-1}$. 通过对各含卤阻燃剂的降解产物毒性推测,说明 UV/CI 体系中产生的 RCS 与 $\cdot\text{OH}$ 攻击了键能较低的位点,被快速有效降解. 因此, UV/CI 体系对含卤阻燃剂具有高效的降解效果,同时降解产物的毒性较产物本身普遍降低.

3 结论(Conclusion)

(1) 该研究通过 Gaussian 09 软件和 Mutiwfn 程序对 3 种典型的含卤阻燃剂 (TCBPA、TBBPA、DBDPE) 的键能与 Fukui 指数进行计算,进而通过比较分析各化学键位的断裂势,推测出各降解路径和产物.

(2) ECOSAR 软件是评估降解产物水生毒性效应的有效可靠预测工具. 该研究通过 ECOSAR Version 2.0 (2000-2016 U.S. Environmental Protection Agency) 软件对含卤阻燃剂的降解产物进行毒性预测与分析,得出阻燃剂降解产物的毒性均低于阻燃剂母体的评估结果,说明通过 UV/CI 体系降解含卤阻燃剂可有效降低潜在的环境危害.

(3) 尽管采用模型与软件对阻燃剂的降解路径和毒性预测不能完全代替实验分析,但通过非实验测试的方法不仅能够研究提供简便有效的路径方法,实现对含卤阻燃剂及其他持久毒害性有机污染物降解机理和产物毒性快速预测.

参考文献 (References)

- [1] 朱冰清, 史薇, 胡冠九, 等. 中国海洋环境中卤代阻燃剂的污染现状与研究进展 [J]. 环境化学, 2017, 36(11): 2408-2423.
ZHU B Q, SHI W, HU G J et al. The pollution status and research progress on halogenated flame retardants in China marine environment [J]. Environmental Chemistry, 2017, 36(11): 2408-2423 (in Chinese).
- [2] 童艺, 程伊雪, 吴冠履, 等. 新型溴系阻燃剂环境污染现状研究进展 [J]. 环境化学, 2021, 40(1): 83-101.
TONG Y, CHENG Y X, WU G Y, et al. Current research progress on environmental pollution of novel brominated flame retardant [J]. Environmental Chemistry, 2021, 40(1): 83-101 (in Chinese).
- [3] LIU W T, PAN Y F, YANG L, et al. Developmental toxicity of TCBPA on the nervous and cardiovascular systems of zebrafish (*Danio rerio*): A combination of transcriptomic and metabolomics [J]. Journal of Environmental Sciences, 2023, 127: 197-209.
- [4] WANG S T, LI W L, CHEN Y Y, et al. Toxicity evaluation of decabromodiphenyl ethane (DBDPE) to *Pleurotus ostreatus*: Oxidative stress, morphology and transcriptomics [J]. Journal of Hazardous Materials, 2022, 431: 128625.
- [5] YAO Y R, YIN L, HE C, et al. Removal kinetics and mechanisms of tetrabromobisphenol A (TBBPA) by HA-n-FeS colloids in the absence and presence of oxygen [J]. Journal of Environmental Management, 2022, 311: 114885.
- [6] 朱婧文, 耿存珍, 张丽珠, 等. 溴系阻燃剂的环境毒理学研究进展 [J]. 环境科技, 2012, 25(5): 62-67.
ZHU J W, GENG C Z, ZHANG L Z, et al. Progress on environmental toxicology of brominated flame retardants [J]. Environmental Science and Technology, 2012, 25(5): 62-67 (in Chinese).
- [7] 高玉娟, 谢承劫, 余虹, 等. 溴代阻燃剂在土壤中的迁移转化研究进展 [J]. 环境科学研究, 2021, 34(2): 479-490.
GAO Y J, XIE C J, YU H, et al. Research progress on migration and transformation of brominated flame retardants in soil [J]. Research of Environmental Sciences, 2021, 34(2): 479-490 (in Chinese).
- [8] 徐建林, 王涛, 康成虎, 等. 阻燃剂研究与应用进展及问题思考 [J]. 材料导报, 2022, 36(10): 235-243.
XU J L, WANG T, KANG C H, et al. Research and applications of flame retardants: A review and thoughts [J]. Materials Reports, 2022, 36(10): 235-243 (in Chinese).
- [9] 王爽, 路珍, 李斐, 等. 典型溴系阻燃剂四溴双酚A和十溴二苯乙烷的污染现状及毒理学研究进展 [J]. 生态毒理学报, 2020, 15(6): 24-42.
WANG S, LU Z, LI F, et al. A review of pollution status and toxicological researches of typical brominated flame retardants tetrabromobisphenol A (TBBPA) and decabromodiphenyl ethane (DBDPE) [J]. Asian Journal of Ecotoxicology, 2020, 15(6): 24-42 (in Chinese).
- [10] 高佳楠, 王树涛, 齐虹, 等. 4种类型土壤中十溴二苯乙烷的光降解行为 [J]. 环境科学与技术, 2021, 44(10): 66-74.
GAO J N, WANG S T, QI H, et al. Photodegradation of decabromodiphenyl ethane in four different soils [J]. Environmental Science & Technology, 2021, 44(10): 66-74 (in Chinese).
- [11] 李海燕. 广州城市污水厂中卤系阻燃剂和污泥重金属研究 [D]. 广州: 广州大学, 2015.
LI H Y. Study of HFRs and heavy metals in municipal sewage treatment plant in Guangzhou [D]. Guangzhou: Guangzhou University, 2015 (in Chinese).
- [12] WANG J, CHEN S J, NIE X, et al. Photolytic degradation of decabromodiphenyl ethane (DBDPE) [J]. Chemosphere, 2012, 89(7): 844-849.
- [13] 范荣桂, 魏来, 张泽伟, 等. 水中典型溴系阻燃剂的降解与测定方法 [J]. 应用化工, 2020, 49(8): 2116-2121.
FAN R G, WEI L, ZHANG Z W, et al. Degradation and determination method of typical bromine flame retardant in water [J]. Applied Chemical Industry, 2020, 49(8): 2116-2121 (in Chinese).

- [14] 刘舒巍, 杨兴桐, 张从轩, 等. 氯系阻燃剂四氯双酚A的毒性及降解技术研究进展 [J]. 化工环保, 2017, 37(2): 145-151.
LIU S W, YANG X T, ZHANG C X, et al. Research progresses on ecotoxicology and degradation technology of tetrachlorobisphenol-a as chlorine flame retardant [J]. Environmental Protection of Chemical Industry, 2017, 37(2): 145-151 (in Chinese).
- [15] 孙家宁, 孙韶华, 宋娜, 等. 高级氧化技术去除水中溴系阻燃剂的研究进展 [J]. 工业水处理, 2022, 42(2): 19-26.
SUN J N, SUN S H, SONG N, et al. Research progress of advanced oxidation technology to remove brominated flame retardants from water [J]. Industrial Water Treatment, 2022, 42(2): 19-26 (in Chinese).
- [16] 郭耀广. 基于光化学高级氧化技术降解水中典型卤代酚类污染物的研究 [D]. 上海: 东华大学, 2014.
GUO Y G. Photochemical advanced oxidation processes-based degradation of typical halogenated organic phenolic pollutants in water [D]. Shanghai: Donghua University, 2014 (in Chinese).
- [17] 张静, 严静娜, 郭悦宁, 等. 阻燃剂四溴双酚A的厌氧-好氧生物降解 [J]. 环境化学, 2016, 35(9): 1776-1784.
ZHANG J, YAN J N, GUO Y N, et al. Anaerobic and aerobic biodegradation of flame retardant tetrabromobisphenol A [J]. Environmental Chemistry, 2016, 35(9): 1776-1784 (in Chinese).
- [18] DONG H Y, QIANG Z M, HU J, et al. Degradation of chloramphenicol by UV/chlorine treatment: Kinetics, mechanism and enhanced formation of halonitromethanes [J]. Water Research, 2017, 121: 178-185.
- [19] PAN M W, WU Z H, TANG C Y, et al. Emerging investigators series: Comparative study of naproxen degradation by the UV/chlorine and the UV/H₂O₂ advanced oxidation processes [J]. Environmental Science: Water Research & Technology, 2018, 4(9): 1219-1230.
- [20] YEOM Y, HAN J R, ZHANG X R, et al. A review on the degradation efficiency, DBP formation, and toxicity variation in the UV/chlorine treatment of micropollutants [J]. Chemical Engineering Journal, 2021, 424: 130053.
- [21] HUA Z C, LI D, WU Z H, et al. DBP formation and toxicity alteration during UV/chlorine treatment of wastewater and the effects of ammonia and bromide [J]. Water Research, 2021, 188: 116549.
- [22] ZHOU Y J, CHENG F Y, HE D Y, et al. Effect of UV/chlorine treatment on photophysical and photochemical properties of dissolved organic matter [J]. Water Research, 2021, 192: 116857.
- [23] 程艳, 陈会明, 于文莲, 等. QSAR技术对高关注化学物质生态环境毒理风险预测 [J]. 环境科学研究, 2009, 22(7): 817-822.
CHENG Y, CHEN H M, YU W L, et al. Eco-environmental toxicity risk prediction for substances of very high concern with QSAR approach [J]. Research of Environmental Sciences, 2009, 22(7): 817-822 (in Chinese).
- [24] YIN R, BLATCHLEY E R 3rd, SHANG C. UV photolysis of mono- and dichloramine using UV-LEDs as radiation sources: Photodecay rates and radical concentrations [J]. Environmental Science & Technology, 2020, 54(13): 8420-8429.
- [25] DEMIRCIOĞLU Z, ALBAYRAK KAŞTAŞ Ç, BÜYÜKGÜNGÖR O, et al. The spectroscopic (FT-IR, UV-vis), Fukui function, NLO, NBO, NPA and tautomerism effect analysis of (E)-2-[(2-hydroxy-6-methoxybenzylidene)amino]benzonitrile [J]. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2015, 139: 539-548.
- [26] LU T, CHEN F W, et al. Multiwfn: A multifunctional wavefunction analyzer [J]. Journal of Computational Chemistry, 2012, 33(5): 580-592.
- [27] GEERLINGS P, de PROFT F, LANGENAEKER W, et al. Conceptual density functional theory [J]. Chemical Reviews, 2003, 103(5): 1793-1874.
- [28] ZACHARIAS A O, VARGHESE A, AKSHAYA K B, et al. DFT, spectroscopic studies, NBO, NLO and Fukui functional analysis of 1-(1-(2, 4-difluorophenyl)-2-(1H-1, 2, 4-triazol-1-yl)ethylidene) thiosemicarbazide [J]. Journal of Molecular Structure, 2018, 1158: 1-13.
- [29] BELFIELD S J, ENOCH S J, FIRMAN J W, et al. Determination of “fitness-for-purpose” of quantitative structure-activity relationship (QSAR) models to predict (eco-) toxicological endpoints for regulatory use [J]. Regulatory Toxicology and Pharmacology, 2021, 123: 104956.
- [30] WANG J J, QIN J Z, LIU B J, et al. Reaction mechanisms and toxicity evolution of Sulfamethoxazole degradation by CoFe-N doped C as Electro-Fenton cathode [J]. Separation and Purification Technology, 2022, 298: 121655.
- [31] LI Z Y, WANG F, ZHANG Y M, et al. Activation of peroxymonosulfate by CuFe₂O₄-CoFe₂O₄ composite catalyst for efficient bisphenol a degradation: Synthesis, catalytic mechanism and products toxicity assessment [J]. Chemical Engineering Journal, 2021, 423: 130093.
- [32] FAN Y J, YANG J, CAI K C, et al. Mechanism of 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide degradation in UV light-emitting diodes lamp driven sodium sulfite activation process [J]. Process Safety and Environmental Protection, 2022, 165: 704-715.
- [33] HEGER S, BRENDT J, HOLLERT H, et al. Green toxicological investigation for biofuel candidates [J]. Science of the Total Environment, 2021, 764: 142902.
- [34] MA C, LIU X G, WU X H, et al. Kinetics, mechanisms and toxicity of the degradation of imidaclothiz in soil and water [J]. Journal of Hazardous Materials, 2021, 403: 124033.
- [35] ZHU Y X, ZHENG Y Q, JIAO B, et al. Photodegradation of enestroburin in water by simulated sunlight irradiation: Kinetics, isomerization, transformation products identification and toxicity assessment [J]. Science of the Total Environment, 2022, 849: 157725.
- [36] LIU W, LI Y Y, LIU F Y, et al. Visible-light-driven photocatalytic degradation of diclofenac by carbon quantum dots modified porous g-C₃N₄: Mechanisms, degradation pathway and DFT calculation [J]. Water Research, 2019, 151: 8-19.
- [37] WAN D, WANG H Y, POZDNYAKOV I P, et al. Formation and enhanced photodegradation of chlorinated derivatives of bisphenol A in wastewater treatment plant effluent [J]. Water Research, 2020, 184: 116002.
- [38] GUO Y G, ZHOU J, LOU X Y, et al. Enhanced degradation of Tetrabromobisphenol A in water by a UV/base/persulfate system: Kinetics and intermediates [J]. Chemical Engineering Journal, 2014, 254: 538-544.
- [39] CHEN J, XU X X, PAN X X, et al. Mechanism insights into the oxidative degradation of decabromodiphenyl ethane by potassium permanganate in acidic conditions [J]. Chemical Engineering Journal, 2018, 332: 267-276.
- [40] LI C G, ZUO J L, LIANG S J, et al. Photodegradation of decabromodiphenyl ethane (DBDPE) adsorbed on silica gel in aqueous solution: Kinetics, products, and theoretical calculations [J]. Chemical Engineering Journal, 2019, 375: 121918.