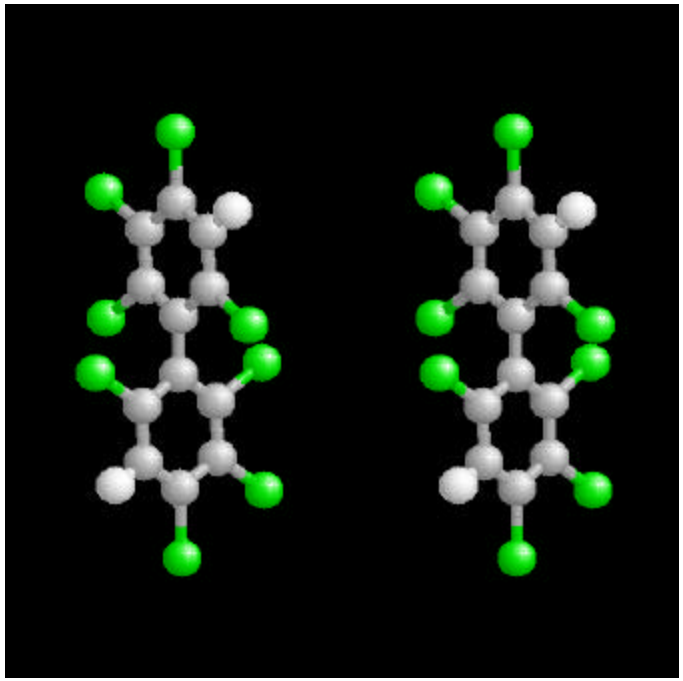
Destruction of Polychlorinated Biphenyls in Acoustically Cavitating Systems



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Polychlorinated Biphenyls
Extent and Significance of Contamination
Regulatory Issues

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- PCBs are present at U. S. Department of Energy sites[1]
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- The EPA has set a maximum contaminant level of 0.0005 mg/L PCBs for drinking water[2]
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- PCBs have been detected at ~383 of the 1,430 National Priorities List sites identified by the U. S. Environmental Protection Agency (EPA)[3]
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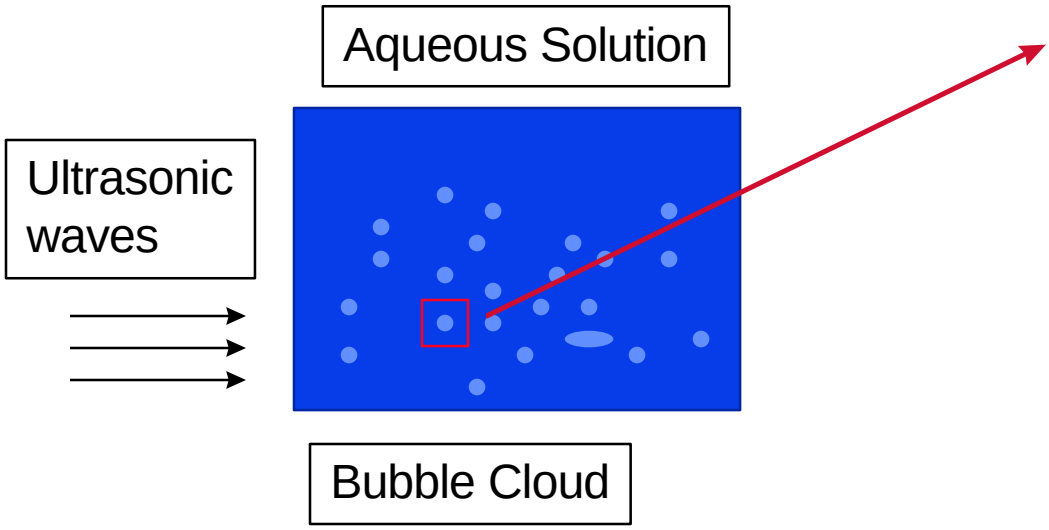
- Manufacture of PCBs halted in the United States in 1977[3]

1. U.S. Department Of Energy Office of Environmental Management Oak Ridge Operations Technology Needs Database URL: http://www.em.doe.gov/techneed/index.html
2. "MANAGEMENT OF POLYCHLORINATED BIPHENYLS IN THE UNITED STATES " Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency URL: http://www.em.doe.gov/techneed/index.html
3. ATSDR-ToxFAQs Agency for Toxic Substance and Disease Registry URL: http://atsdr1.atsdr.cdc.gov:8080/tfacts17.html

Selected Current Technologies and Approaches

1. Incineration (1,200 ^{o} C - 1,600 ^{o} C) 2. Bioremediation 3. Fe^{3+} /H_2O_2/ UV
4. γ-Ray Destruction 5. **Ultrasonic Irradiation**



- T = 2000 - 4000 K within individual microbubbles
- Pyrolysis Reactions
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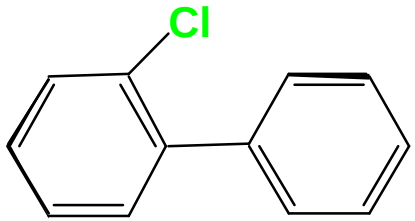
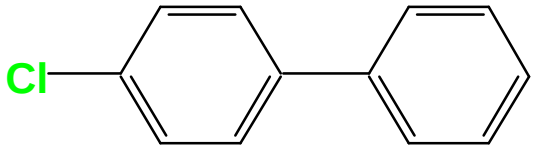
- Free-radical reactions
-
- Decomposition of numerous organic pollutants

Selected Congeners: Physico-Chemical Properties

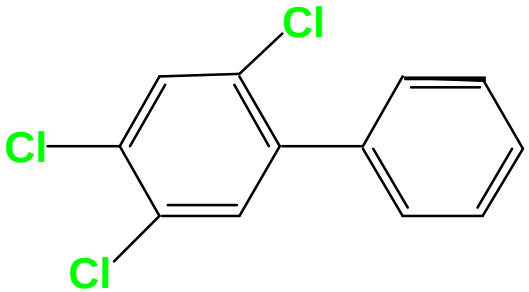


2-chlorobiphenyl



4-chlorobiphenyl

PCB	MW, g/mol	Boiling Point, ^{o} C	Vapor Pressure, Pa, 25 ^{o} C	Octanol/Water Partition Coefficient (Log K_{ow})
2-CBP	188.65	274	< 1.8	4.5
4-CBP	188.65	285	< 1.4	4.8
2,4,5-CBP	257.54	--	< 0.132	5.8



2,4,5-trichlorobiphenyl

Project Objectives

- Measure the decomposition rate of aqueous PCBs under different reactor conditions

- Determine the influence of ultrasonic frequency

- Determine the chlorine atom balance

- Detect organic free-radicals with Electron Spin Resonance (ESR)

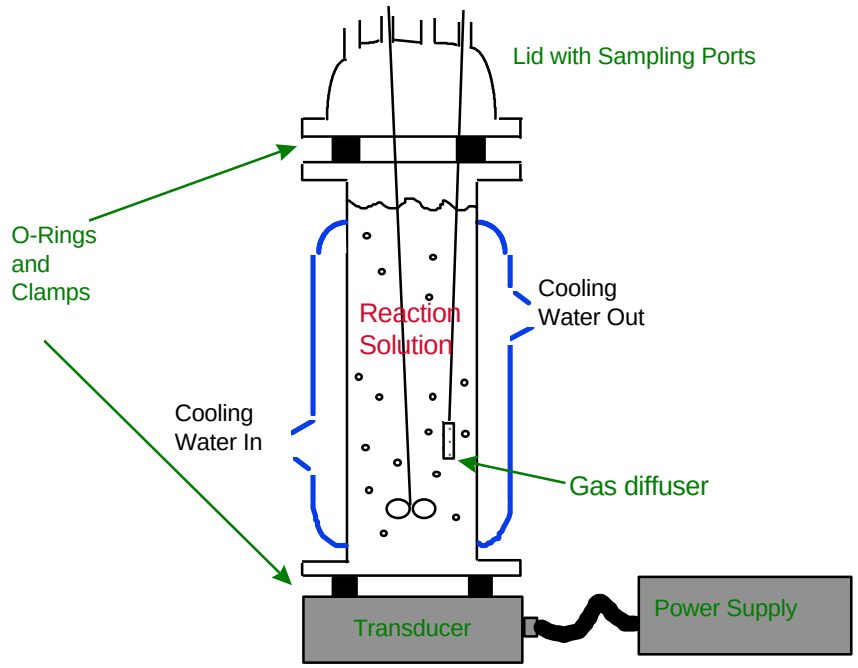
- Identify major reaction products with Gas Chromatography/Mass Spectroscopy
-
- Desirable end-products include **Cl^-**, short-chain carboxylic acids, CO_2 (key: aromatic ring rupture)

Experimental Methods

Reactor Configurations

Ultrasonic Frequency:
205, 358,618, 1071 kHz
Sonicated volume: 400 mL

**Studies also conducted at 20 kHz - probe reactor



Analytical Techniques

- GC/ECD and GC/MS - identification and quantification of PCBs and PCB break-down products
- Ion Chromatography - detection of chloride ion
- Electron Spin Resonance - Identification of Organic Free Radicals

Experimental Data and Results

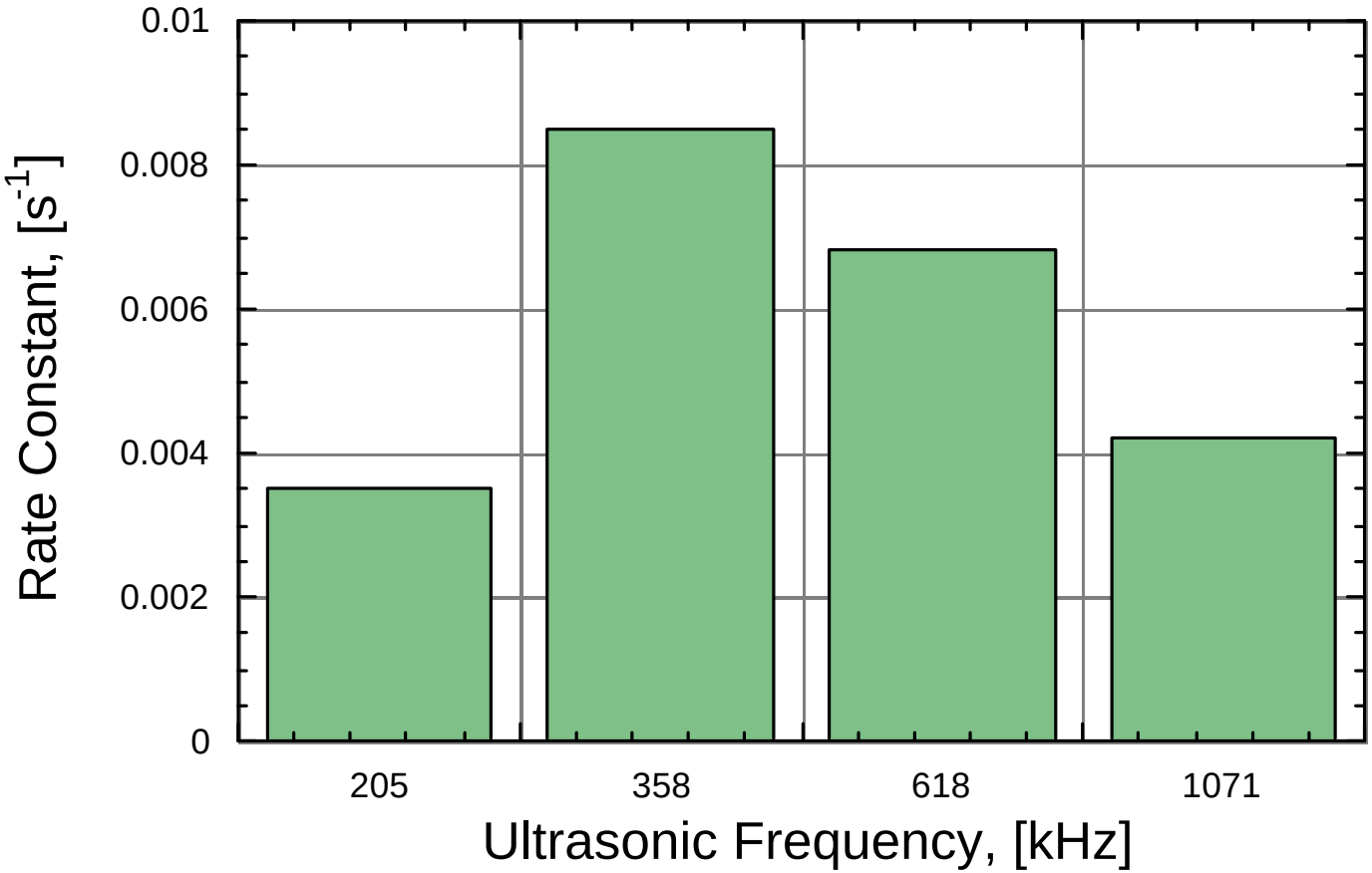
Table 1: Degradation rates of PCBs

Congener	Fre-quency, kHz	Concentration µmol L^{-1}	Sparge gas	First order rate constant (s^{-1}) x 10^3	Standard deviation
2-PCB	20	3.4	Ar	2.9	1.2%
2-PCB	20	4.6	Ar	2.1	1.35%
2-PCB	20	10.4	Ar	0.89	0.13%
2-PCB	20	26.1	Ar	0.27	0.4%
2-PCB	205	5.2	Ar	3.6	2.5%
2-PCB	358	5.2	Ar	8.5	4.67%
2-PCB	618	5.2	Ar	7.6	1.98%
2-PCB	1071	5.2	Ar	4.1	3.0%
4-PCB	20	5.4	Ar	1.6	2.11%
245PCB	20	0.076	Ar	2.6	3.62%
245PCB	20	0.076	O_2	2.1	2.97%
245PCB	20	0.077	Ar:O_2 (1:1)	3.5	4.03%
245PCB	20	0.076	Ar:O_2 (4:1)	3.8	5.31%

Previous investigations indicate that the saturating gas, initial substrate concentration, and ultrasonic frequency can significantly impact the rate of pollutant decomposition. Thus, these variables were examined during sonication of selected PCB congeners.

Experimental Data and Results

Significance of Ultrasonic Frequency

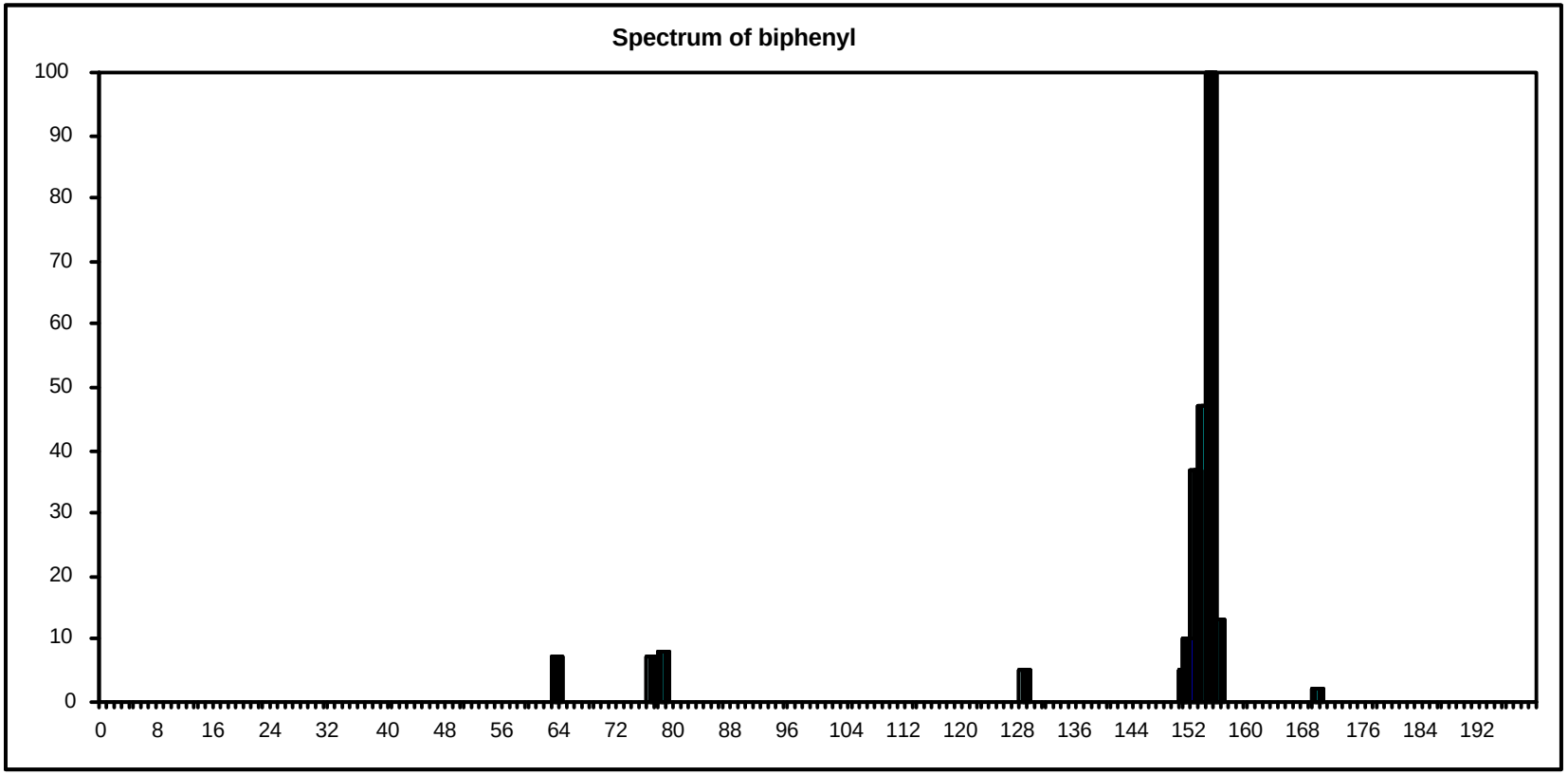


- The decomposition rate of 2-PCB is optimal at 358 kHz (Ar gas sparge)
- 99% destruction would require 9 minutes
- Chloride recovery also varies with ultrasonic frequency:

72-83% recovery as chloride ion over the frequency range 205 - 1017 kHz

Mass Spectroscopy Studies

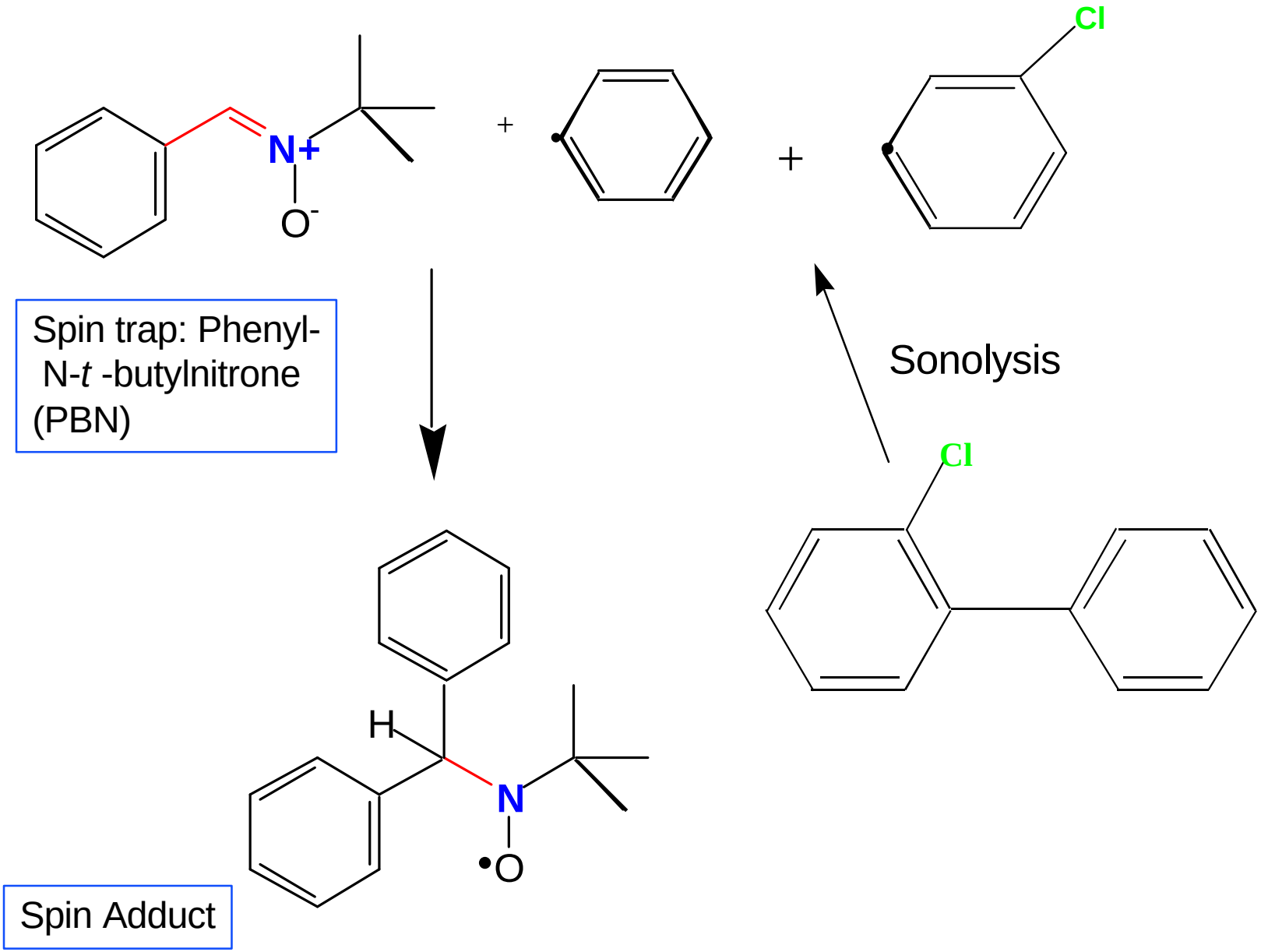
Detecting Biphenyl



•Sonication of 2-PCB (Ar sparge, 20 kHz) yielded by-products which include biphenyl. The above spectrum was taken for a sample of sonicated PCB solution and compared to a library spectrum for 2-PCB.

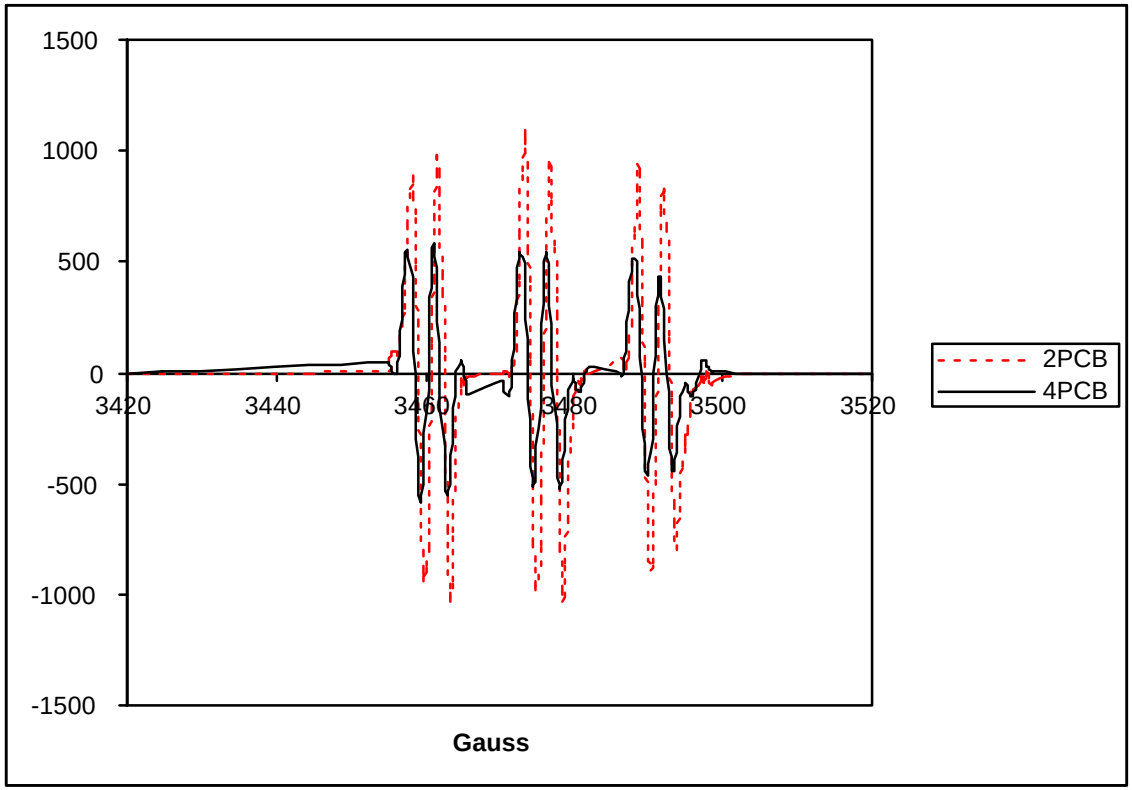
•Detection of biphenyl indicates that dechlorination occurs readily during the sonolytic decomposition of 2-PCB.

ESR Detection of Phenyl Radical by Spin-Trapping



Electron Spin Resonance and Spin-Trapping

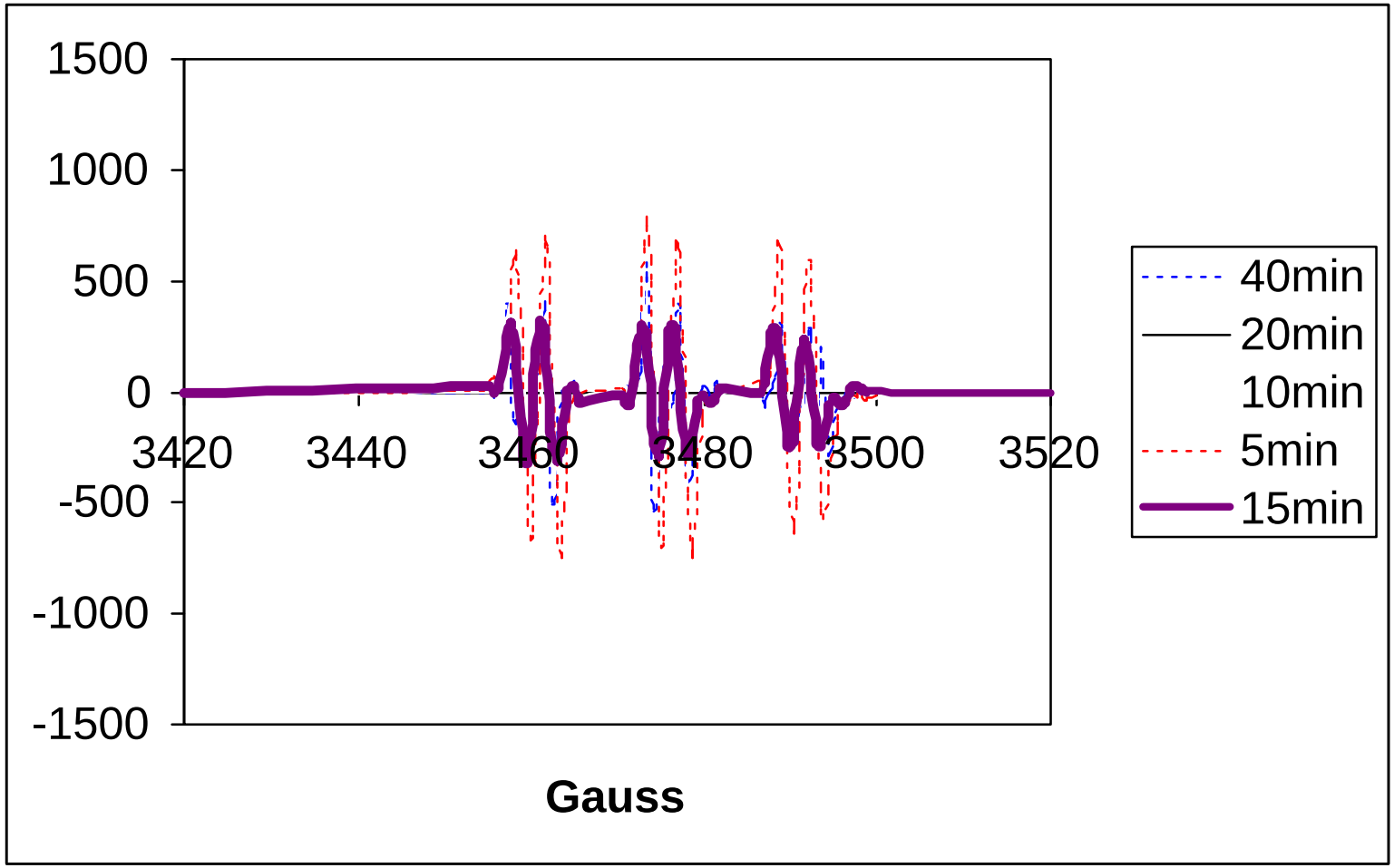
First Derivative Spectra



The formation of phenyl radical during the sonolysis of 2-PCB and 4-PCB was confirmed by spin-trapping separate solutions of each congener. Note that after 10 minutes of ultrasonic irradiation, the intensity is higher for 2-PCB than for 4-PCB, which corresponds to the faster rate of 2-PCB decomposition (see Table 1).

Electron Spin Resonance and Spin-Trapping

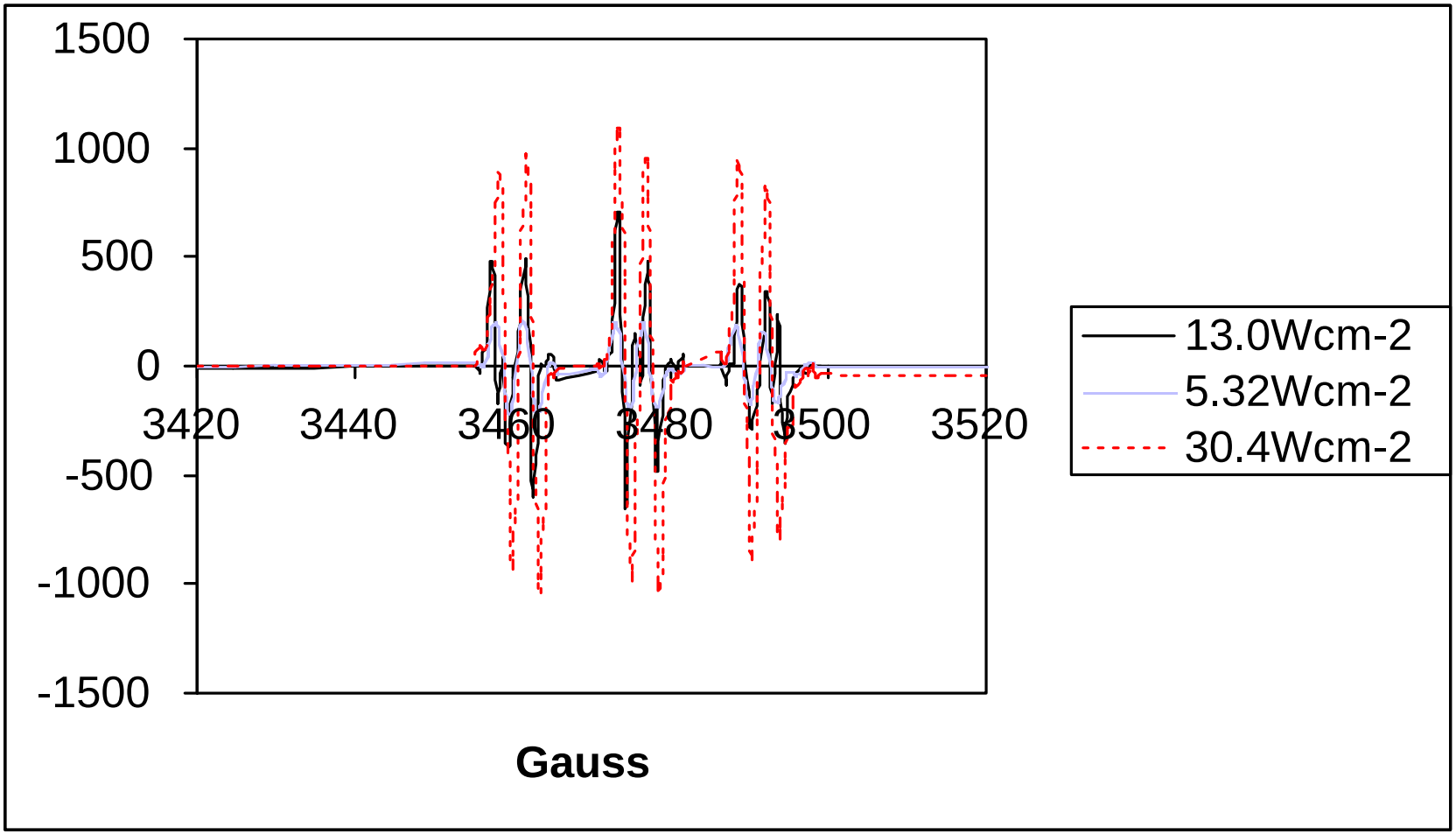
First Derivative Spectra



Time variation of PBN-phenyl spin-adduct during sonication of 2-PCB (20 kHz, Ar sprage). The spin-adduct initially accumulates, corresponding to formation of phenyl radical from the destruction of 2-PCB.

Electron Spin Resonance and Spin-Trapping

First Derivative Spectra



Variation of PBN-phenyl peak area with variable ultrasonic intensity (2-PCB, 20 kHz, Ar-sparge). The greater peak area at higher intensities corresponds to faster observed kinetics during sonication. The impact of sound intensity on sonochemical kinetics has been previously reported, and was also confirmed by ESR in this study with PCBs.

Summary and Conclusions

1. Bench scale studies indicate that ultrasonic irradiation effectively destroys aqueous PCBs.

2. 358 kHz is an optimal ultrasonic frequency for PCB decomposition.

3. Rapid dechlorination occurs during sonolysis and is confirmed by the detection of biphenyl with GC/MS.

4. ESR studies with the spin-trap PBN confirm the formation of phenyl radical, indicating rupture of the carbon-carbon bond between the phenyl rings.

5. Peak areas corresponding to the spin-adduct vary with congener structure, the sound intensity, and the duration of irradiation.

6. The experimental observations indicate that thermolysis is a primary transformation pathway during PCB destruction. Thus, further optimization of ultrasonics for pollutant destruction should involve reactor configurations and solution conditions which enhance thermolytic pathways.

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6. The experimental observations indicate that pyrolysis is a primary transformation pathway during PCB sonolysis.

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