An Investigation of Homogeneous and Heterogeneous Sonochemistry for the Destruction of Hazardous Substances

submitted by

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Introduction and Background

The preservation and restoration of water quality is a contemporary issue within environmental engineering which is supported by a broad-cross section of Federal agencies. The General Accounting Office reports that 72 federal programs directly or indirectly administer projects related to water quality improvement or protection. An estimated 5.1 billion dollars was requested or appropriated for these efforts in 1996. The Departments of Transportation. Defense. and Agriculture, as well as the Environmental Protection Agency and the National Science Foundation are among the agencies with specific programs. Thus, research in this area occurs from fundamental as well as from applied perspectives.

The issue of water quality fits into the broader realm of aqueous waste stream and land site remediation. Legislation such as the Clean Water Act and the Comprehensive Environmental Response and Liability Act (CERCLA) have mandated the elimination of water and land pollution. Effective control and remediation methods must be developed and implemented to accomplish these tasks. The need for new technology is further driven by the large number of polluted sites across the country. For example, there are currently 3700 sites requiring clean-up within the Department of Energy (DOE) complex, approximately 14,900 sites in progress within the Department of Defense (DOD) and more than 1200 Superfund Sites on the National Priorities List (NPL).

New treatment technology is necessitated by the drawbacks of current control techniques. For instance, the cost of incineration can be prohibitive for dilute waste streams and the impact of incineration emissions on human health has been scrutinized. although incineration is the standard method for destroying highly toxic compounds. This report contains a detailed description of work in progress with a new technology for water pollution control, ultrasonic irradiation. Three ultrasonic reactor systems, and the sonochemistry of environmentally relevant organic compounds, will be discussed.

Cavitation and Ultrasonic Irradiation

Cavitation is defined as the growth and collapse of bubbles in liquids, and can be induced under a variety of physical conditions in water, organic solvents, and biological systems. In

laboratory systems, bubble clouds are induced by ultrasonic irradiation. Ultrasound refers to sound waves with a frequency greater than 16-20 kHz. Applications of ultrasonics are visible in a number of diverse fields, including cleaning, plastics welding, and biological cell disruption. Ultrasonic irradiation has become an important tool for chemists; sonication accelerates reaction rates, enhances heterogeneous catalysis and allows for milder solution conditions.

Acoustic cavitation is induced by ultrasonic waves which impose a sinusoidal pressure variation on the transmitting medium, alternately compressing the liquid molecules or pulling them apart by overcoming intermolecular forces. At an ultrasonic frequency of 20 kHz, the liquid will undergo 2×10^4 compression and rarefaction cycles each second. Microscopic bubbles grow in size during the "rarefaction" half-cycle of the sound wave, and collapse violently during the compression half-cycle. The bubbles occur in clouds within the solution, although the lifetime of a single bubble is on the order of microseconds and its radius is on the order of micrometers. It has been estimated that the bubble density in cavitating solutions is $-10 \times 10^9 \, L^{-1} min^{-1}$.

Extreme temperature and pressure gradients occur within the bubble during cavitational collapse. The maximum temperature, T_{max}, and pressure, P_{max}, at the center of an adiabatically collapsed bubble containing both gas and vapor can be estimated from Eqns. (1) - (2).

$$T_{max} = T_o \left\{ \frac{P_m(K-1)}{P} \right\} \tag{1}$$

$$P_{max} = P \left\{ \frac{P_m(K-1)}{P} \right\}^{\left(\frac{K}{K-1} \right)} \tag{2}$$

where P_m = pressure in the liquid at the time of collapse, P = pressure in the bubble at its maximum size, To = bulk liquid temperature. K is the polytropic index of the gas, and indicates how much heat is released from the gas during adiabatic compression. The predicted temperature and pressure at the center of a collapsed, nitrogen filled bubble in water are 4200 K and 975 atm the bulk liquid remains at ambient conditions. Experimentally, a range of temperatures during bubble implosion has been observed: 2000-4000 K in aqueous solution. The bubble interiors are

under such extreme conditions that light is emitted from cavitating bubbles, a phenomenon known as sonoluminescence. The gas-phase at the center of the bubble, the interfacial layer, and the bulk solution comprise distinct regions in which multiple reaction pathways exist (Fig. 1). Carbon tetrachloride and *p*-nitrophenol arc depicted in the most likely regions of degradation during bubble implosion.

Combustion and pyrolysis reactions occur in the vapor-phase of the bubble. An important reaction is thermolysis of water molecules:

$$H_2O \rightarrow {}^\bullet OH + {}^\bullet H \qquad (3)$$

Hydroxyl radical (${}^\bullet OH$) can attack organic solutes, or recombine to form hydrogen peroxide (H_2O_2). The concentration of hydroxyl radical at the bubble interface has been estimated to be 4×10^{-3} M [Gutiérrez, 1991 #33]. Both oxidants can diffuse into the bulk solution and attack solutes which are not transported to the cavitation bubble. Oxygen atoms are also produced if dissolved oxygen gas is present [Hart, 1986 #82]. In the interfacial region, reactions in supercritical water [Hua, 1995 #37] have been implicated. The supercritical phase of water exists above the critical temperature, T_c, of 647 K and the critical pressure, P_C, of 221 bar and has physical characteristics intermediate between those of a gas and a liquid. Enhanced combustion and hydrolysis of organic compounds has been observed in supercritical water.

The sonochemistry of a large number of chemical compounds of environmental interest in aqueous solutions has been studied. For example, complete decomposition of the pesticide parathion (*O,O*-diethyl *o-p*-nitrophenyl thiophosphate) was observed after two hours of sonication. The sonolytic degradation of the pesticides atrazine and alachlor has also been reported. Exposure of a 100 μM solution of pentachlorophenol (PCP, a widespread pollutant) to ultrasonic irradiation results in a 99% concentration reduction after 100 min and the formation of Cl- (90% theoretical yield after 150 min sonication). Inorganic compounds and heavy metals in aqueous solution (e.g.. thallium, iron, tin) can be oxidized during sonolysis. Hydrogen sulfide, commonly found in sewage streams, appears to be degraded primarily by pyrolytic decomposition.

Ultrasonic irradiation has been applied to other problems of environmental relevance such as sludge de-watering, disinfection, and fossil fuel treatment. It has been applied to large-scale industrial systems as well, such as the cleaning of jet-engine parts.

Project Descriptions and Accomplishments

The primary objective of this research project is to acquire a deeper fundamental knowledge of acoustic cavitation and cavitation chemistry, and in doing so, to ascertain how ultrasonic irradiation can be more effectively applied to environmental problems.

Four on-going projects will be described in this progress report, The first project is the destruction of carbofuran in a Near-Field Acoustical Processor (NAP), and the hydrodynamic characterization of the reactor. The second project is a comprehensive study of how ultrasonic frequency influences sonochemical reaction rates; the substrate it, the preliminary portion of this study has been hydrogen peroxide formation. The third project in progress is destruction of four polychlorinated biphenyls at 20 kHz. Work so far has been at 20 kHz, but the most significant portion of this project will involve a multi-frequency (ultrasonic frequency) study. Finally, the destruction of a pesticide, dichlorvos, during sonication at 500 kHz will be described. Preliminary work during the first year has emphasized determination of kinetics; further work (years 2-3) will be focused upon closing mass balances and identifying transformation products.

• Destruction of Carbofuran in the Near-Field Acoustical Processor

Materials and Methods

Carbofuran (Aldrich, 99%+) and Carbofuran phenol (Aldrich, 99%+) were used as received. Solutions of Carbofuran were made with water obtained from a Barnsted NANOpure ultrapure water system ($R = 18.3$ MΩcm^{-1}). All experiments were performed on 7 L of either 130 μM Carbofuran or 25 μM Carbofuran in water. Solutions were saturated with the appropriate gas (flow rate 50 - 200 ml/min) by bubbling the gas through three glass fritted dispersion tubes (Kontes, New Jersey), which were immersed into the liquid, for at least 20 min before and during sonication. Argon and a mixture of O_2 and Ar were used as the saturating gases.

Once the solution was saturated with the appropriate gas, a t = 0 sample (10 mL) would be taken, and sonication would be started. During sonication, samples (10 mL) of solution were taken from the reservoir every 30 minutes and filtered through a 0.2 μm PFTE filter (Gelman). A Coming 320 pH meter was used to measure pH during experiments.

The degradation of Carbofuran and its hydrolysis product Carbofuran phenol was followed with a Waters liquid chromatograph (HPLC) with a photodiode array detector at a wavelength of λ = 278 nm. A 100 μl sample was injected into a 250×4.6 mm MetaSil Carbamate Column (MetaChem) and eluted with an isocratic program of 40% Acetonitrile (Aldrich, HPLC-grade) and 60% water for 20 minutes. Calibration standards of Carbofuran (ranging from 185 μM to 1 μM) and Carbofuran phenol (ranging from 150 μM to 1 μM) were made with nanopure water and analyzed with the HPLC so that a calibration curve according to the expected concentration range could be obtained.

In a near-field acoustical processor (Advanced Sonic Processing Systems) (Fig. 2) the vibrational energy is transferred to the reaction mixture via two parallel stainless steel plates that are bolted together. Each plate is driven by magnetostrictive transducers that are bonded onto each plate. The total sonoactive area is 1045.16 cm^2, and the length and width are 67.5 and 7.5 cm, respectively. A stainless steel spacer is placed between the two vibrating plates and sealed by a Goretex gasket. So far, spacers at two thicknesses have been employed to study the apparent reaction rate as a function of volume (660.4 and 165.1 mL) and thus of different power-to-volume densities. Power input into the two frequency-generating units was maintained at 1800 W for all experiments. The NAP system allows for direct cooling of the plates and transducers so that the reaction mixture can be hold at constant temperature (20°C). Water is cooled and circulated through the transducer covers by a Fisher Scientific refrigeration unit. A Kimax glass vessel holding up to 10 L of reactant solution is used as a reservoir and closed by a top lid. Various ports in the top lid allow for purging of the reaction mixture with the background gases during an

experiment as well as temperature measurement and sample withdrawal. NAP and reservoir are connected by corrugated Teflon tubing (3/8 inch i.d.).   The reaction mixture is continuously circulated through the system via a peristaltic pump (Masterflex Model) operating with Viton tubing. Throughout the study, a volumetric flow rate of 3.2 L min^{-1} was maintained.

Preliminary characterization of the reactor hydrodynamics involved the use of a conservative tracer (NaCl). The conservative tracer was introduced into the NAP during operation in the flow-through mode (Q = 3.2 L/min), and the spatial and temporal distribution of the tracer was monitored with a conductivity meter (Cole-Parmer, Model #19820-10). Tracer tests were run during ultrasonic irradiation (P = 1800 W) as well as with a "silent" reactor (P = 0).   During the experiments at P = 0 W, the in-flow was switched from tap water (conductivity = 737 μS) to the salt solution (710 mg L^{-1}) at t = -20 seconds: at which time sampling of the outflow was also begun. After 20 seconds, the in-flow was switched back to tap water for another 58 seconds. During experiments at P = 1800 W, the switch from tap water to salt water occurred at t = -30 seconds (at which time sampling of the outflow began), and then switched back to tap-water at t = 0 for an additional 48 seconds. Sampling of the outflow (for both P = 0 W and P = 1800 W) occurred every 2 seconds into disposable borosilicate glass tubes (Fisher).   The gap-width for this preliminary hydrodynamic study was l/8 inch.

Results and Discussion
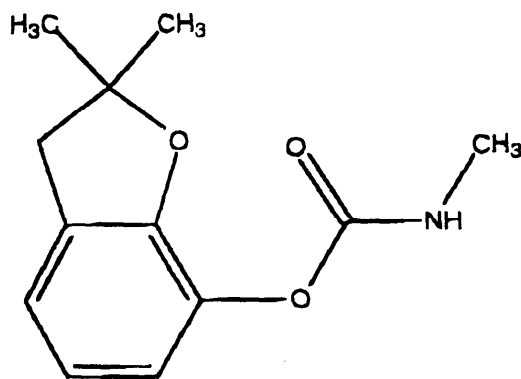
Carbofuran

The destruction kinetics of carbofuran are demonstrated in Figs. 5-7; and the distribution of the tracer with respect to time is show in Fig. 8. All rate constants are larger at the smaller (1/8") gap-width, corresponding to a sono-active volume of 165.1 mL. Carbofuran is destroyed most quickly with an Ar/O$_2$ sparge mixture and during irradiation through the l/8" gap-width. The rate of substrate disappearance under these conditions was 1.48 µM s^{-1}. There is an approximately three-fold increase in the disappearance rate when the gap-width is decreased from l/2" to l/8". This corresponds to a decrease in the power-to-volume ratio from 10.9 W/mL to 2.72 W/mL. The initial concentration of the substrate also influences the disappearance rate. An initial concentration of 25 µM results in an approximately three-fold increase in disappearance rate during irradiation with a l/8" gap-width. However, this trend is not observed with the l/2" gap-width. Further experiments with a larger number of gap-widths should yield a more conclusive trend with respect to initial substrate concentration.

Further work with carbofuran will include Total Organic Carbon (TOC) measurements to determine the; extent of mineralization, as well as analysis with Ion Chromatography (IC). The transformation rates will be further optimized.

- *Ultrasonic Frequency and Hydrogen Peroxide Production*

  Materials and Methods

Ultrapure water was obtained from a NANOpure system (Barnstead) and had a minimum resistance of 18.0 mΩ.. All chemicals [NaOH (Mallinckrodt); potassium biphthalate (Baker): ammonium molybdate (Fisher); KI (VWR Scientific)] were reagent grade and used as received. Compressed gases [Ar; O_2] were provided by AIRCO and BOC gases, respectively.

Sonolyses were performed at four individual frequencies [205, 358,618, or 1071 kHz] with one of two USW 51 Ultrasonic Transducers and an RF power generator [250W $\times$ 0.04 - 1.5 MHz] (Allied-Signal ELAC Nautik) set at 50% power (Fig. 3). Each transducer could be set to two different frequencies, allowing a total of four frequencies. A constant temperature water jacket (15°C) around the reactor was maintained with a refrigerated bath and circulator (Fisher Scientific). The solution was spargcd both for twenty minutes prior to and during the sonolysis with a coarse gas dispersion tube (Kimble Glass, Inc.). Temperatures of the solution were measured with a type J thermocouple (Digi-Sense). The concentration of H_2O_2, in the reactor was determined spectrophotometrically.

The solution was prepared by filling the reactor with 500 ml of the ultrapure water and sparging (either argon or oxygen at 100 ml min^{-1}) for twenty minutes prior to sonication. Samples (0.5 ml to 2.0 ml) from the reactor were diluted with ultrapure water to 2.0 ml and mixed with 1.0 ml 0.1 M potassium biphthalate and 0.75 ml of a solution containing 0.4 M KI, 0.06 M NaOH, and -2$\times$10^{-4}M ammonium molybdate. A treated sample then was placed in a quartz cuvette (1.0 cm path length) and its absorbency was measured. with a UV160-U UV-visible recording spectrophotometer (Shimadzu) at λ = 352 nm.

Results and Discussion

The average rate of H_2O_2 formation as a function of ultrasonic frequency is shown in Figs. 9-10. The complete data set is included in Table I-II. The data can be semi-quantitatively interpreted. For both O_2 and Ar saturated solutions, production of H_2O_2 is faster at 205 and 358 kHz than at 618 or 1071. Hydrogen peroxide production was measured in order to provide baseline information about the functional dependence of sonochemical reactions on ultrasonic

frequency. The exact correlation and optimal frequency of a reactor for treatment applications will most likely depend on the specific type of functional group transformation which occurs. H_2O_2 is formed by several pathways during sonolysis, including the recombination of hydroxyl radical:

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$$
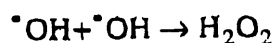
Further work at variable ultrasonic frequencies will include sonication of polychlorinated biphenyls (PCBs) and other organic compounds. An important fundamental study will be the detection of short-lived species in solution, produced either during the sonolysis of pure water or during the sonolysis of aqueous organic compounds.

- *Kinetics of Polychlorinated Biphenyl Destruction at 20 kHz*

  <u>Materials and Methods</u>

  2-chlorobiphenyl, 4-chlorobiphenyl, 2,4,5-chlorobiphenyl, 2,3,4,5,6-chlorobiphenyl were purchased from Accustandard Inc. and used without further purification. Hexane (HPLC grade) was purchased from Fisher Company.

  A high intensity ultrasonic reactor system (Sonics and Materials, Inc.) operating at 20 kHz and with power range of O-400 W was utilized for irradiation of the PCB solutions (Fig. 4). The surface area of the ultrasonic probe was 1.32 cm^2 and the average power intensity = 53W/cm^2.

  2-chloro- and 4-chlorobiphenyl were dissolved directly into water (5 ppm and 1 ppm, respectively) and the solutions were stirred for at least one week before use. Because of their low water solubilities, 2,4, 5-chloro- and 2, 3, 4, 5, 6-chlorobiphenyl were dissolved in hexane and then diluted into water, stirred for at least one week before use; final concentrations were 100 ppb and 20 ppb. Stock solutions of the polychlorinated biphenyls (PCBs) were made in hexane at a concentration of 1000 ppm and dilutions were then made into construct a calibration curve.

  165 ml of solution was added into the reactor, saturated with purging gas (Argon) at 200 ml/min before and during sonication. Magnetic stirring was used during sonication. 5.0 ml samples were withdrawn at appropriate time intervals; the withdrawn volume was replaced with an equal volume of unsonicated PCB solution, in order to keep the volume within the reactor solution

constant during sonication. Samples were extracted into 1 mL hexane and 1 μL was injected into a Hewlett-Packard 5990 Gas Chromatograph equipped with an Electron Capture Detector (ECD) and a Supelco 30m × 0.32μm DBS column.   The temperature program for 2-CBP and 4-PCB was as follows: 120° C - 200° C at 5° C/min. For the higher congeners, $T_{initial}$ = 160° C, 160° 210°C at 5° C/min an isothermal period for 3min. at 210° C.
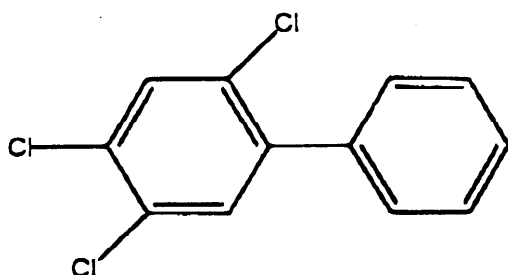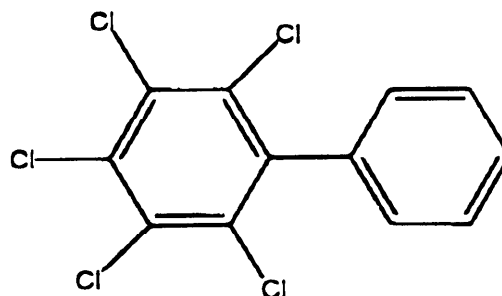
Results and Discussion
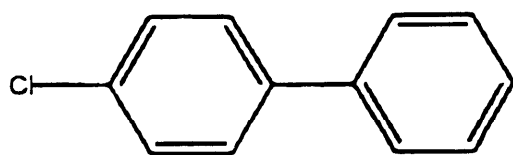
4-chlorobiphenyl
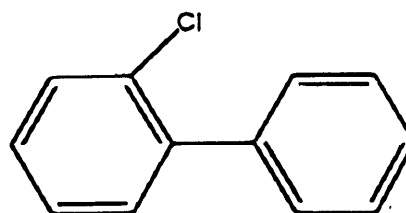
2-chlorobiphenyl

2,4,5-trichlorobiphenyl

2,3,4,5,6-pentachlorobiphenyl

The kinetics of PCB decomposition during sonolysis are demonstrated in Figs. 11-13. The position of the chlorine on a mono-substituted biphenyl has a slight influence on the decomposition rate, as shown in the comparison plot of 2-chlorobiphenyl (2-CBP) and J-chlorobiphenyl (4-CBP) (Fig. 11).   2-CBP appears to decompose more quickly, under identical solution conditions. However, the extent of chlorine substitution is also important.   2,4,5-trichlorobiphenyl is destroyed more rapidly than either of the monosubstituted biphenyls, and 2,3,4,5,6-pentachlorobiphenyl exhibits the slowest decomposition rate (Fig. 12).

In the presence of free-radical scavengers (0.5 mM and 50 mM sodium bicarbonate), the decomposition of 2,4,5-TCB is hindered (Fig. 13). The higher concentration of sodium bicarbonate demonstrates a greater influence on the decomposition rate. Thus, free-radical attack (most likely hydroxyl radical) play an important role in the destruction of a PCB during sonolysis. Further studies of this nature will be done with other congeners.

The physical properties of selected PCBs are compiled in Table III. The high K_{ow} values and low vapor pressure values suggest that PCBs will partition to the cavitation bubble interfacial region and undergo both pyrolytic and free-radical reactions. Additional studies with PCBs include sonication at multiple frequencies, and detection and quantification of chloride **ion** and short chain organic acids, in order to close the carbon and chlorine mass balance. structural identification of intermediates produced during sonication will be obtained with a Gas-Chromatography/Mass Spectrometry (GC/MS) analysis.

- *Sonolysis of Aqueous Dichlorovos at 500 kHz*

    Materials and Methods

Dichlorvos (Supelco) and hexanes (pesticide grade, Fisher Scientific) was used as received. Solutions of dichlorvos were made with water from the Nanopure water system. Each experiment was performed with 800 mL of 0.5 mM dichlorvos solution. The total power output ranged from 90 - 165 W. The UES 500 (Ultrasonic Energy Systems, Panama City, FL) generator and ultrasound transducer were used with a glass vessel (The Custom Glass Shop, Vineland, NJ) for a batch system. The glass vessel had a jacket to allow for cooling with water from a refrigerated circulator (Fisher Scientific). A thermocouple thermometer with a stainless steel probe (Cole Parmer) was used for temperature measurements. A glass fritted diffuser was used to disperse Argon, Oxygen or mixtures of the two gases into the system. The Argon was at a flow rate of 50-100 mL/min (air) and was sparged into the system for at least 20 minutes prior to the experiment as well as during the experiment to allow for saturation with Argon. A Coming 320 pH meter was used to measure pH of the samples during experiments.

Once the solution was saturated with Argon, a zero sample (5 mL) would be taken, and sonication would be started. During sonication, samples were taken every 15 minutes until at least 90% degradation was achieved. Each sample was placed in an 8 mL glass vial and extracted with 2 mL of hexane immediately after sampling. The extraction was agitated for at least 2 minutes to ensure contact between the water and hexane layers.

The analysis was performed with a Hewlett-Packard Model 5890 series II gas chromatograph (GC) with an HP-I. column. One microliter of the hexane layer was injected into the GC with a temperature program of 120 °C for 3 minutes, 10 °C/minute, 150 °C for 3 minutes. Calibration standards with concentrations of 0.5 mM, 0.25 mM, 0.1 mM, 0.05 mM, and 0.01 mM were made with nanopure water, extracted with hexane. and analyzed with the GC so that a calibration curve could be obtained. Once a calibration curve was obtained the areas of the peaks for each sample were correlated to a concentration.

Results and Discussion
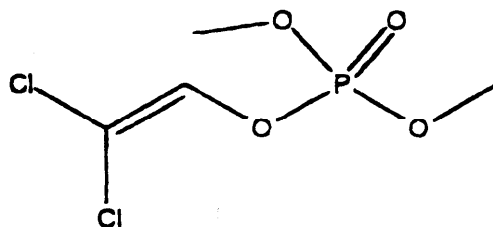
2,2-Dichlorovinyl-O,O-dimethyl phosphate (Dichlorvos)

The influence of the total acoustic power output, and the dissolved gas composition on the decomposition of dichlorvos can be seen in Figs. 14-16. The total acoustic output, varied from 85 W to 160 W also increased the rate as which dichlorvos was destroyed during sonication at 500 kHz (Fig. 14) There is a significant enhancement of the first order decomposition rate constant when a mixture of Ar and O_2 gas is used to saturate the solution (Figs. 15 and 16.). This is consistent with other investigators' results. Subsequent experiments will focus on structural identification of by-products, as well as an exploration of saturating gases, such as air.

Figures and Tables

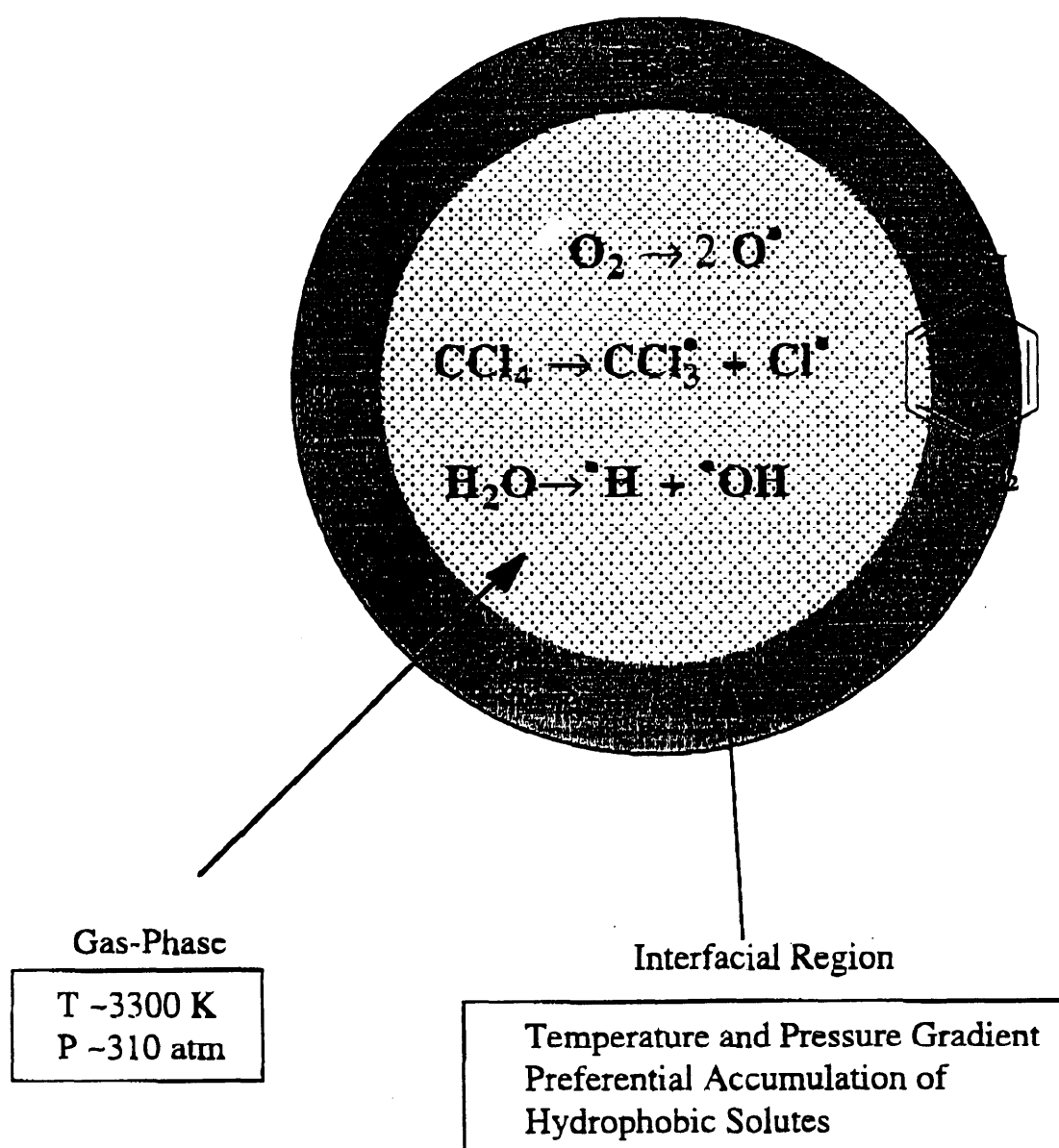Bulk Solution

T = 298 K, P = 1 atm
No concentration gradients

$O_2 \rightarrow 2\,O^{\bullet}$

$CCl_4 \rightarrow CCl_3^{\bullet} + Cl^{\bullet}$

$H_2O \rightarrow {}^{\bullet}H + {}^{\bullet}OH$

Gas-Phase

T ~3300 K
P ~310 atm

Interfacial Region

Temperature and Pressure Gradient
Preferential Accumulation of
Hydrophobic Solutes

Fig. 1: Cavitation bubble in aqueous solution.
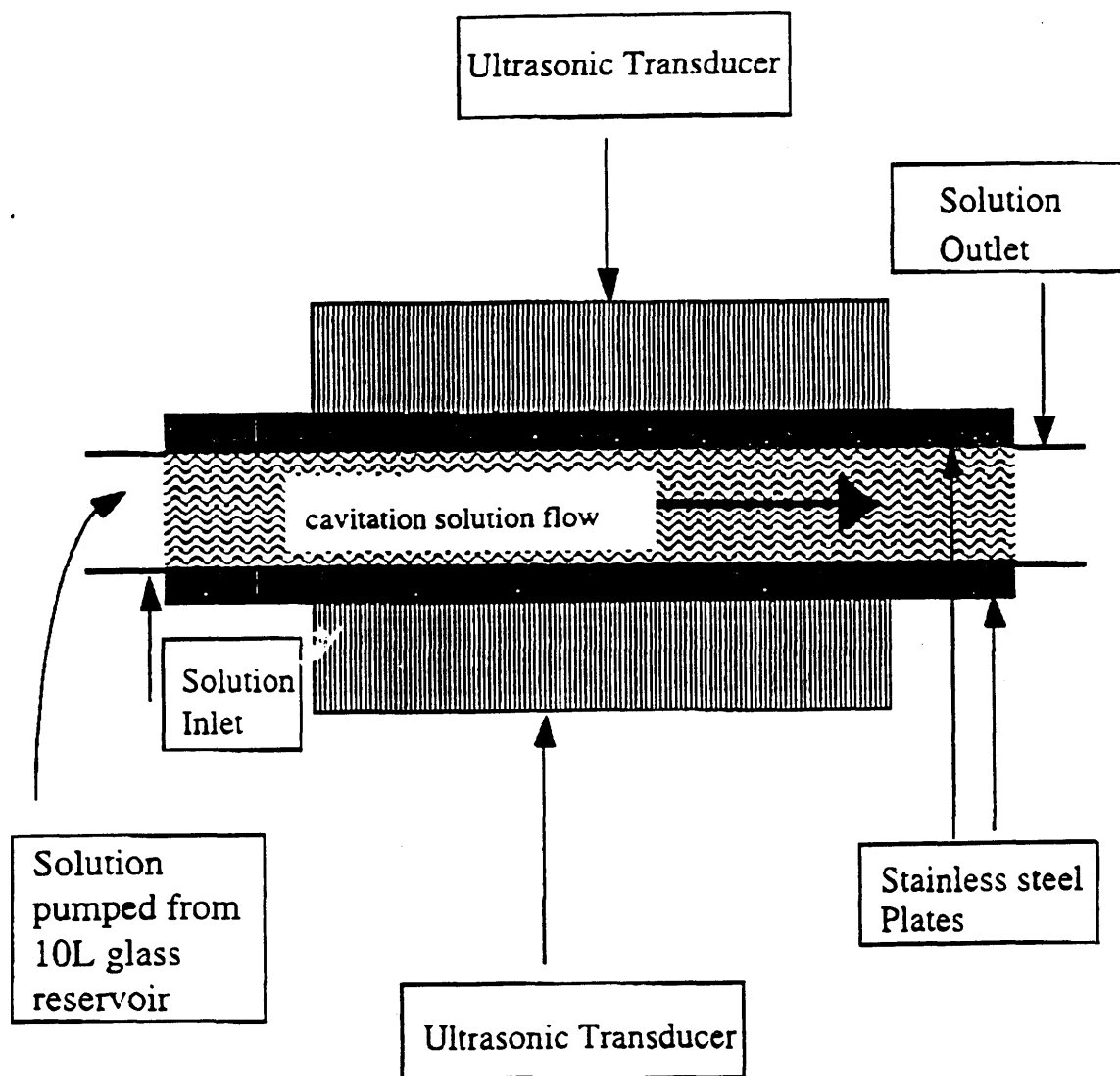
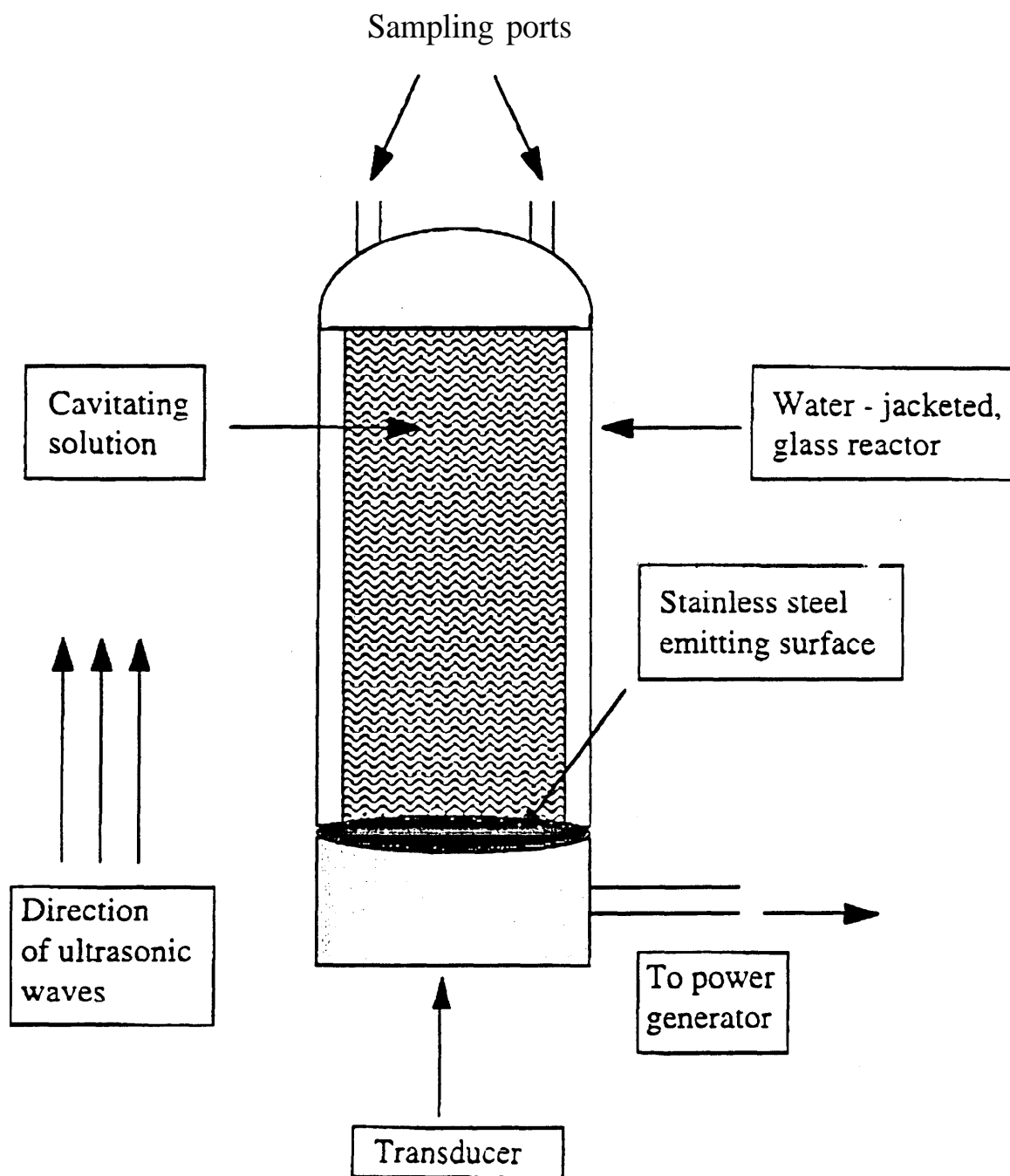Fig. 2: Near-Field Acoustical Processor operating in recycle mode.

Sampling ports

Fig. 3:

Reactor configuration for 500 kHz UES Reactor and the AlliedSignal Multi-Frequency Reactor.

To power generator

Transducer

Ultrasonic Probe

Sampling port

Teflon Collar

Direction of ultrasonic waves

Water-jacketed vessel
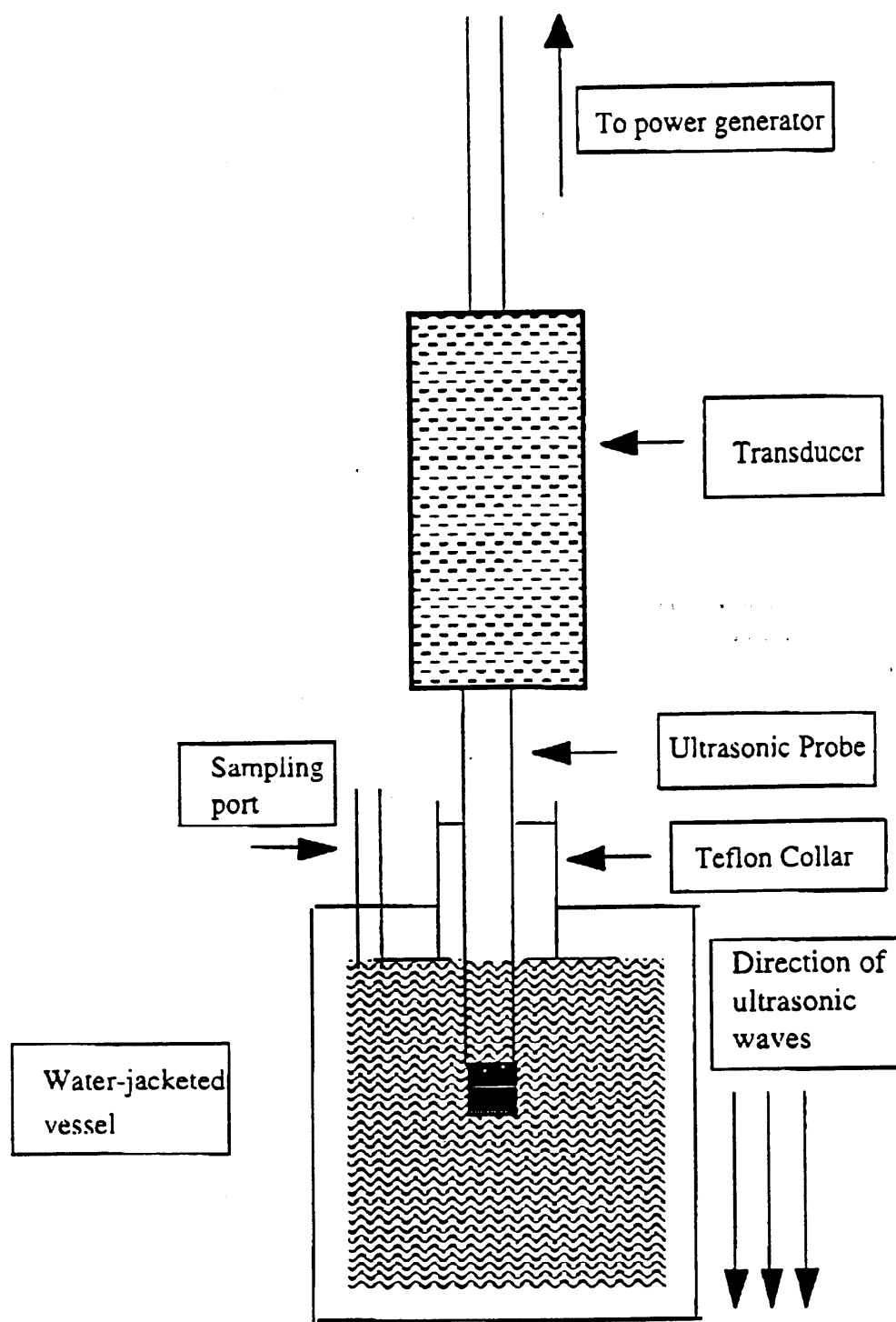
Fig. 4: Ultrasonic probe reactor.
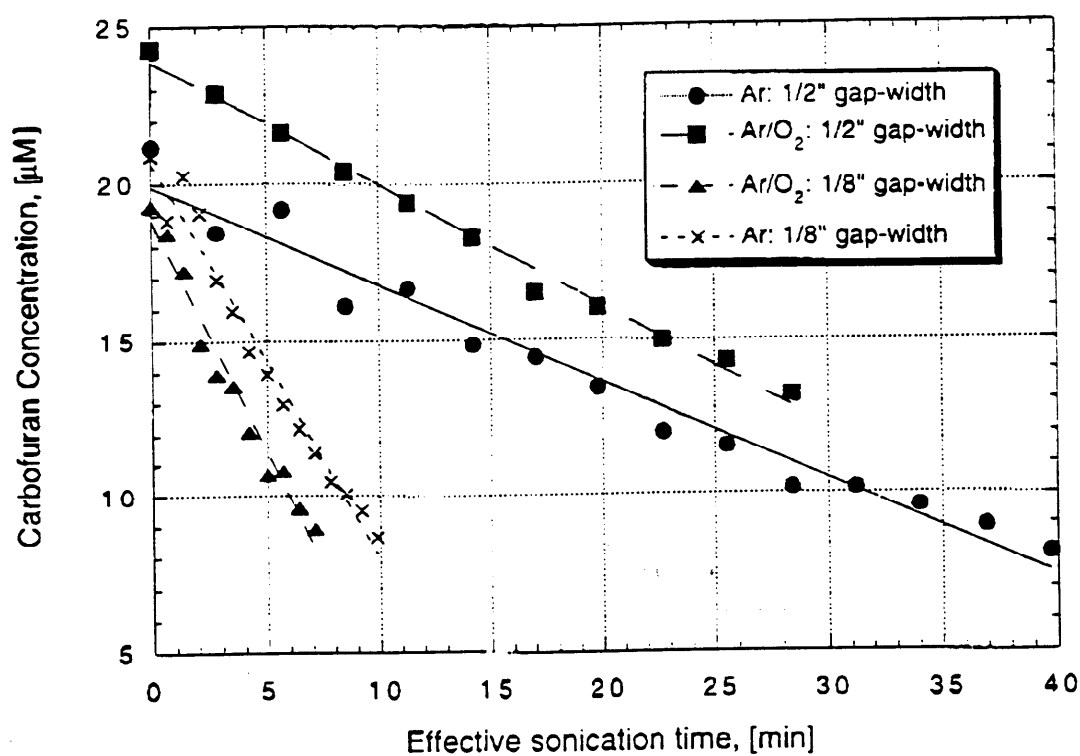
$y = 19.901 - 0.31349x \quad R = 0.98422$

$y = 23.895 - 0.39042x \quad R = 0.99598$

$y = 18.851 - 1.4839x \quad R = 0.98572$

$y = 20.698 - 1.2715x \quad R = 0.9873$

Fig. 5: Decomposition kinetics for aqueous carbofuran. Reaction rate constants range from 0.31 - 1.48 min^{-1}.

Fig. 6: Decomposition kinetics for aqueous carbofuran. Reaction rate constants are larger during sonication at smaller gap-widths.

Fig. 7: Decomposition kinetics for aqueous carbofuran. Reaction rate constants arc larger during sonication at higher acoustic power-to-volume ratios.
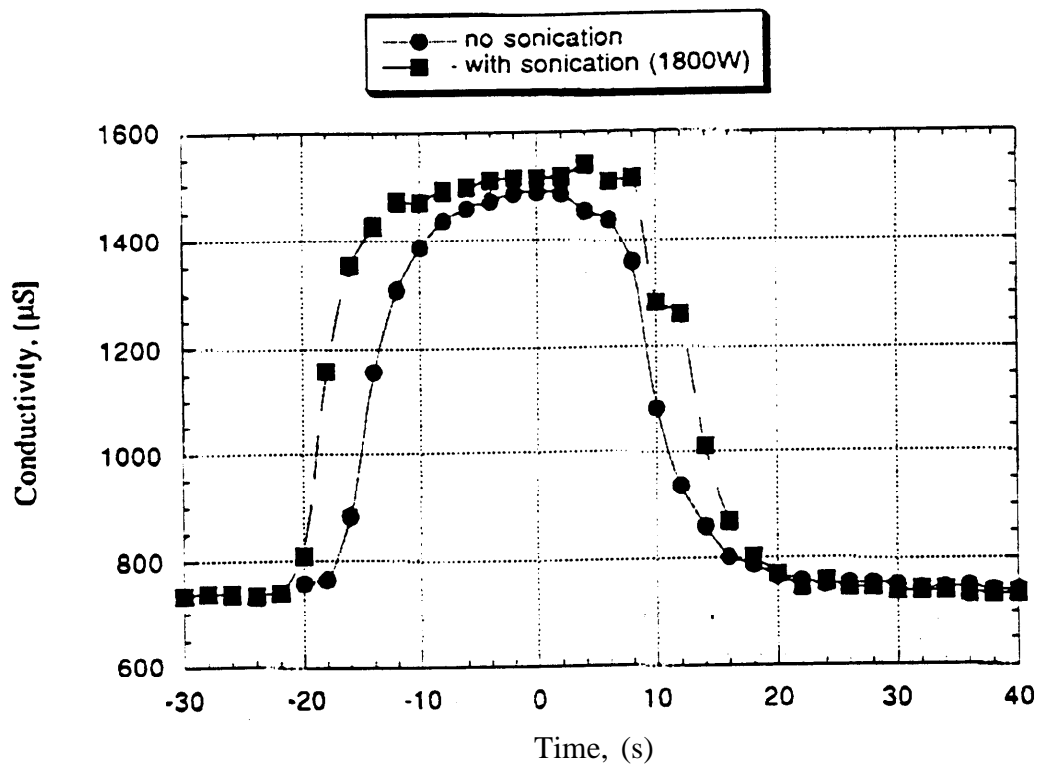
Fig. 8: Distribution of tracer pulse (NaCl) during operation in the flow - through mode, at P = 1800 W or P = 0 W.
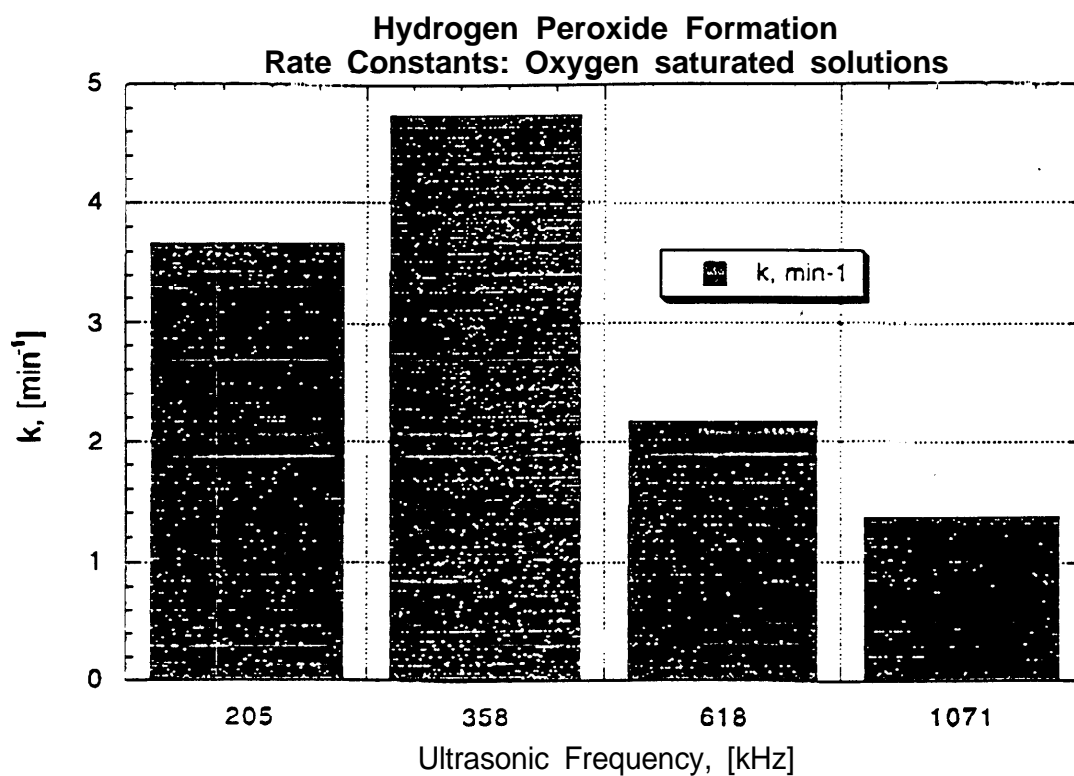
Fig. 9: Optimal ultrasonic frequency for hydrogen peroxide production during sonication of water is 358 kHz. Note: values have been averaged. Numerical data given in Table I.

Hydrogen Peroxide
Formation Rate Constants
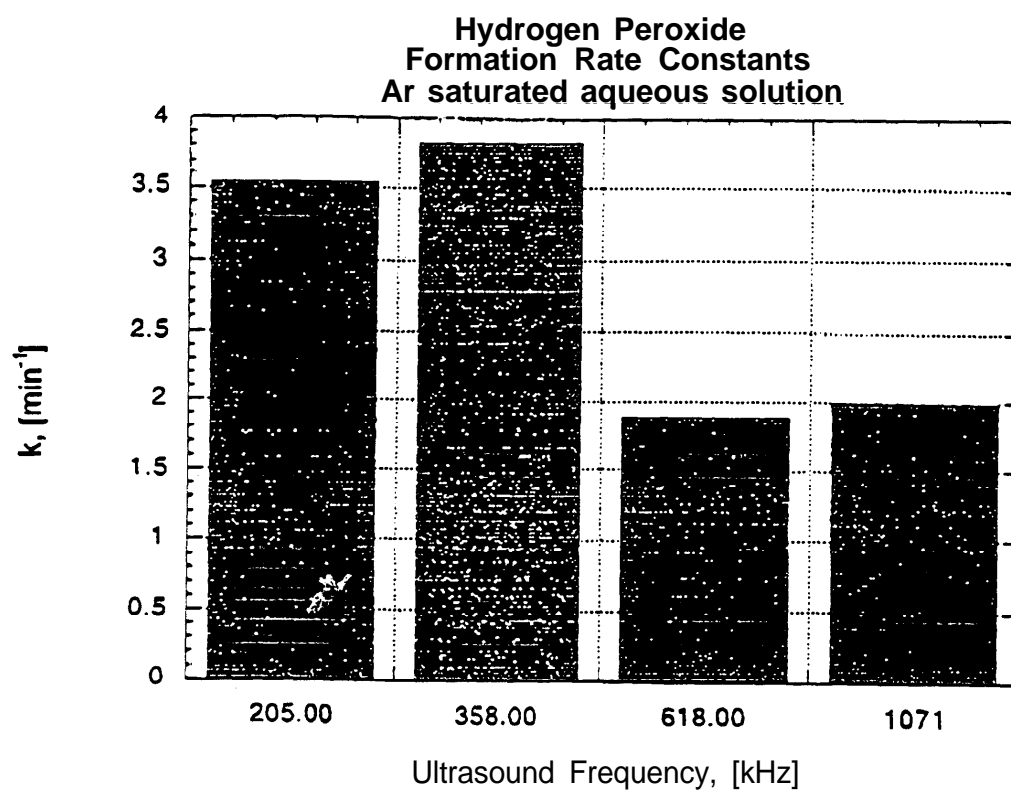**Ar saturated aqueous solution**

Fig. 10: Optimal ultrasonic frequency for hydrogen peroxide production during sonication of water is 358 kHz. Note: values have been averaged. Numerical data given in Table I.
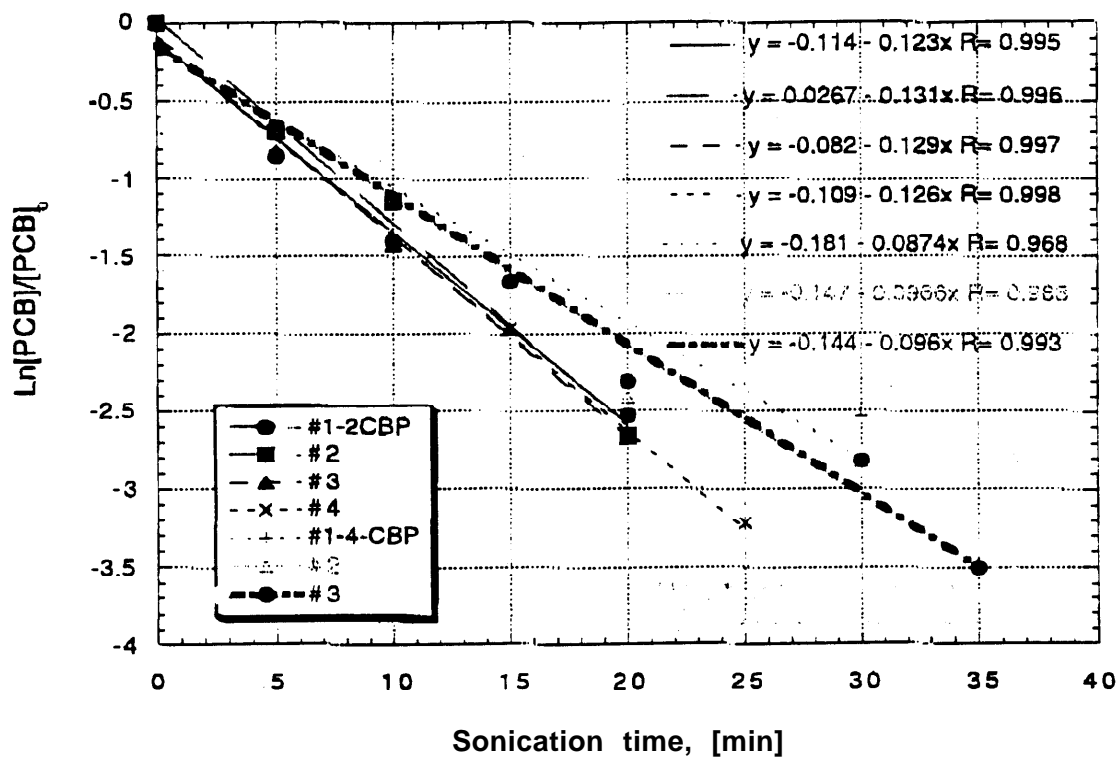
2-CBP and 4-CBP

Fig. 11: Decomposition of 2-chlorobiphenyl and 4-chlorobiphenyl sonicated separately. The 2-chlorobiphenyl exhibits a slightly larger rate constant.
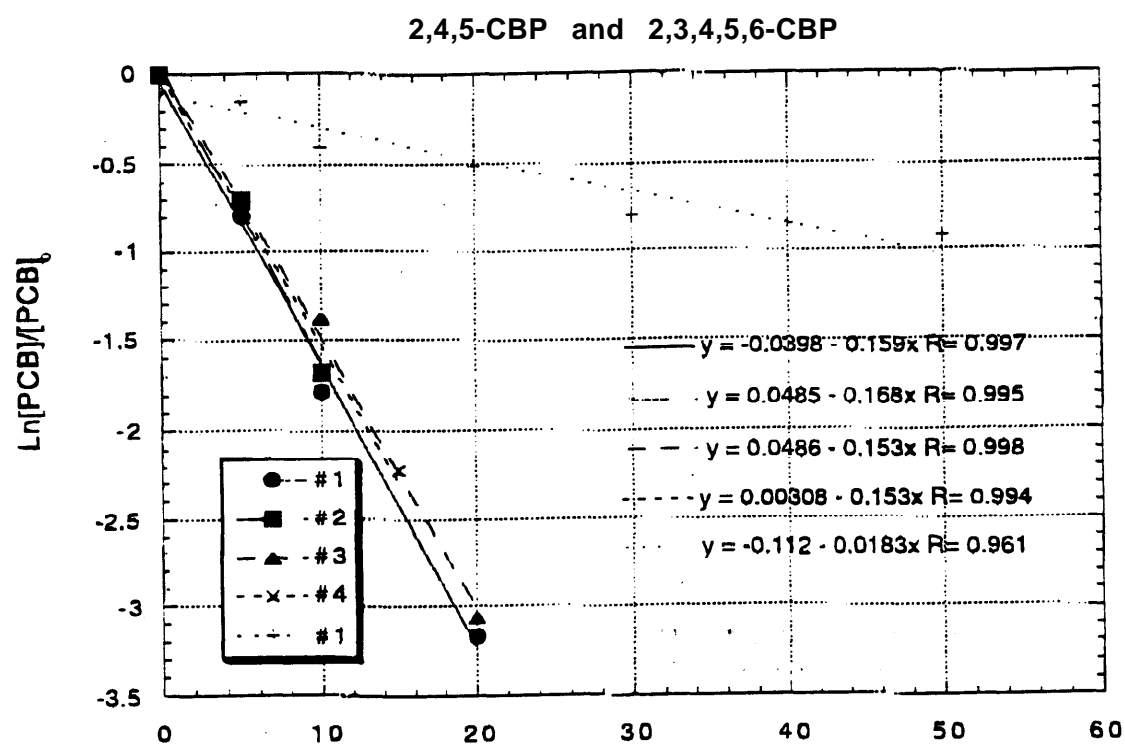
2,4,5-CBP   and   2,3,4,5,6-CBP

Fig. 12: Decomposition of 2,4,5-trichlorobiphenyl and 2,3,4,5,6-pentachlorobiphenyl sonicated separately in Ar-saturated solution.

2,4,5-PCB sonicated with varying concentrations of Sodium Carbonate

Legend on plot:
- $y = 0.026326 - 0.065376x$ R= 0.9746
- $y = -0.073123 - 0.14185x$ R= 0.9958
- $y = -0.056332 - 0.13648x$ R= 0.99519

Y-axis: $\ln[PCB]/[PCB]_0$

X-axis: Sonication time, [min]
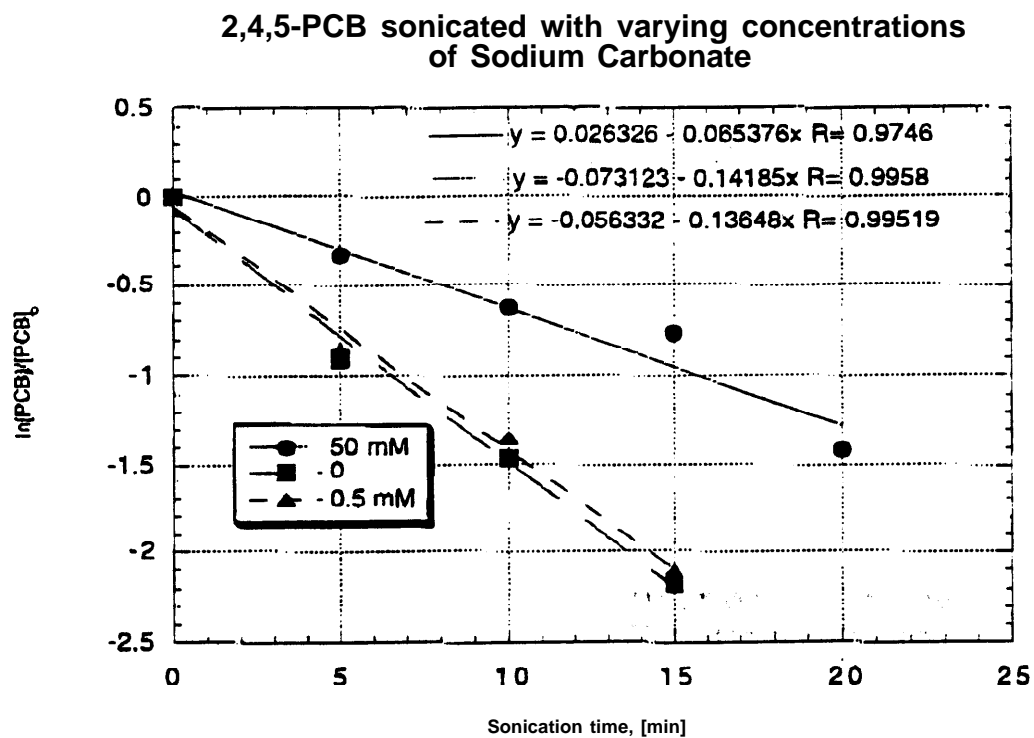
Legend box:
- 50 mM
- 0
- 0.5 mM

Fig. 13: Decomposition of 2,4,5-trichlorobiphenyl in the presence of free-radical scavenger bicarbonate. The decomposition rate constant is largest in the absence of scavengers.
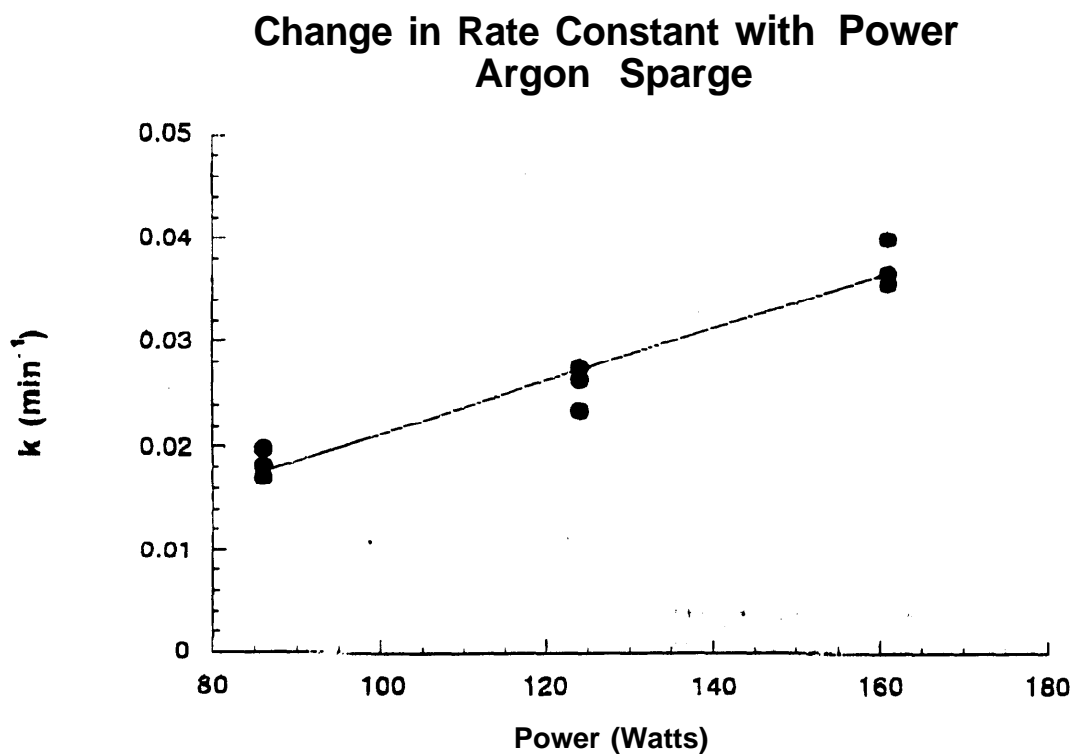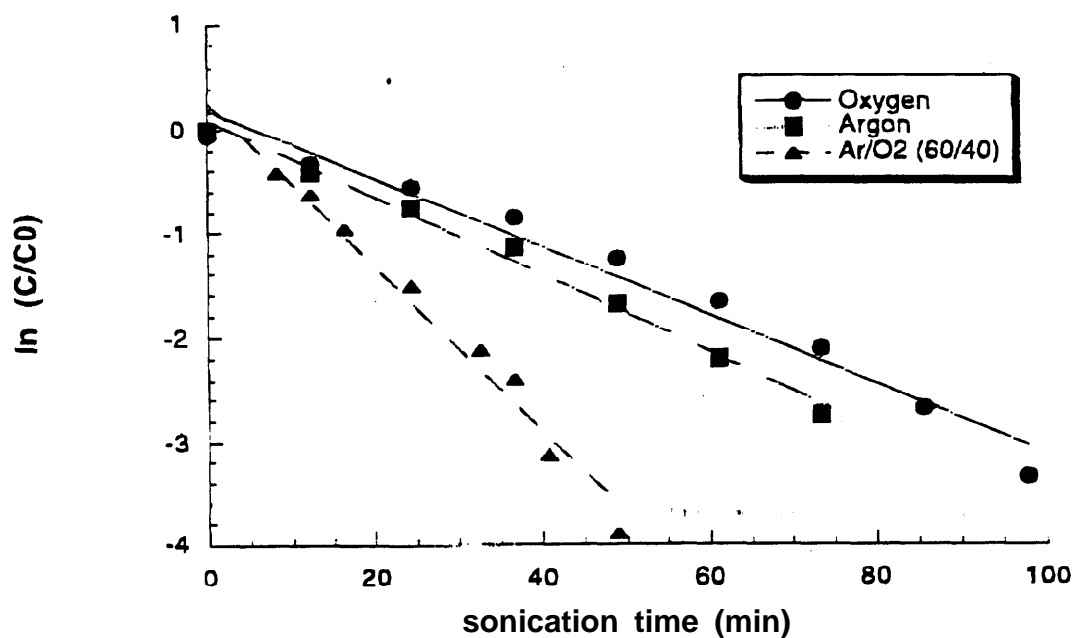
**Change in Rate Constant with Power
Argon Sparge**

Fig. 14: Dichlorovos sonication at 500 kHz. Higher acoustic power results in faster dichlorvos decomposition.

Effect of Sparge Gas on Dichlorvos Degradation Rate

$$y = 0.18956 + -0.033008x \quad R = 0.9865$$

$$y = 0.095192 + -0.037372x \quad R = 0.99587$$

$$y = 0.26362 + -0.079008x \quad R = 0.98804$$

Fig. 15: Dichlorovos sonication at 500 kHz. An optimal decomposition rate constant is obtained during sonication of a solution saturated with a mixture of Ar and O_2.
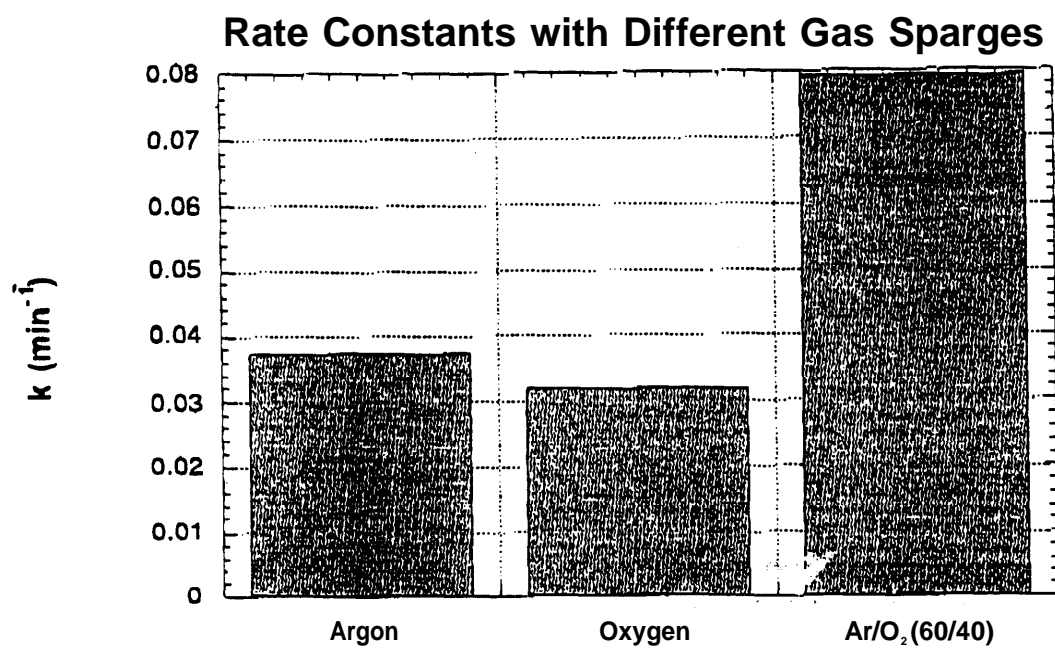
Rate Constants with Different Gas Sparges

Fig. 16: An optimal decomposition rate constant is obtained during sonication of a solution saturated with a mixture of Ar and O_2.

Table I

Rates ($\times 10^6$ M min^{-1}) for Hydrogen Peroxide Production during Sonication

Oxygen Saturated Solution

Run #	205 kHz	358 kHz	618 kHz	1071 kHz
1	3.4	4.58	2.48	1.54
2	4.04	4.12	1.87	1.4
3	3.56	5.52		1.45
4				1.4
5				1.27
6				

Table II

Rates ($\times 10^6$ M min^{-1}) for Hydrogen Peroxide Production during Sonication

Argon Saturated Solution

Run #	205 kHz	358 kHz	618 KHz	1071 kHz
1	3.71	3.93	0.93	2
2	3.23	3.62	1.53	2.01
3	3.64	3.61	1.97	1.96
4	3.6	4.11	2.42	
5		3.86	2.58	
6				

Table III

Physical Properties of Selected Chlorinated and Polychlorinated Biphenyls

PCB	MW, g/mol	Boiling Point, ° C	Vapor Pressure, Pa, 25 ° 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
2,3,4,5,6-CBP	326.43	--	<.0034	6.8