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Project Title: **An Investigation of Homogeneous and Heterogeneous Sonochemistry for Destruction of Hazardous Waste**

Lead Principal Investigator:

Dr. Inez Hua
Environmental Engineering and Hydraulics
Purdue University
1284 Civil Engineering Building
West Lafayette, Indiana 47907-1284
Telephone: 317-494-2409
e-mail: hua@ecn.purdue.edu

An Investigation of Homogeneous and Heterogeneous Sonochemistry for Destruction of Hazardous Waste

Inez Hua, Purdue University

Research Objective

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. The primary objective will be accomplished by examining numerous aspects of sonochemical systems and acoustic cavitation. During the course of the project, the research group will investigate sonochemical kinetics and reactive intermediates, the behavior of heterogeneous (solid/liquid) systems, and the significance of physical variables during sonolysis. An additional component of the project includes utilizing various techniques to image cavitation bubble cloud development.

Research Progress and Implications

This report summarizes results after 3 years of investigation. On-going projects will be summarized in this annual report. Detailed information and results from year 1 and year 2 of this investigation can be found in the publications listed at the end of this report, under the heading “Publications Resulting from This Work”.

a. Spectroscopic Studies of Organic Free-Radicals Resulting from Sonication of Polychlorinated Biphenyls

Cavitation chemistry encompasses complex pathways involving numerous reactive intermediates, and identification of these intermediates is crucial for elucidating the mechanism

of sonochemistry. Free - radicals play an important role in the vapor phase chemistry of the bubble, and also in aqueous reactions. For example, it has been reported that $\bullet\text{CH}_3$, $\bullet\text{CH}_2\text{CH}_2\text{OH}$, and $\bullet\text{CH}_2$ -phenyl were produced during sonication of aqueous methanol, ethanol, and sonication of pure toluene.

In order to identify organic free - radicals present at quantifiable concentrations during the sonication of PCBs, we employed Electron Spin Resonance (ESR) with a spin trap, *N-t*-butyl- α -phenyl-nitron (PBN). PBN reacts with the reactive free - radicals to form more stable spin-adducts, which are then detected by ESR. The ESR spectrum of a PBN spin adduct exhibits hyperfine coupling of the unpaired electron with the ^{14}N and the β -H nuclei which leads to a triplet of doublets. The combination of the spin-adduct peak position and peak interval uniquely identifies the structure of a free-radical.

The first-derivative ESR spectra of 2-PCB and 4-PCB yielded interpretable signals, but no significant peaks were found when analyzing sonicated solutions of 2,4,5-PCB. The formation of organic radicals at a detectable level may have been hindered by the low aqueous solubility of 2,4,5-PCB.

Figure 1 is an ESR spectrum acquired after 10 minutes of sonicating an Ar - saturated solution of 2-PCB and PBN at 20 kHz. Samples that were irradiated at different power intensities for the same time period (10 minutes) are compared. Peaks consist of a triplet of doublets with the parameters of $\alpha_{\text{H}} = 4.2$, $\alpha_{\text{N}} = 16.0$, which are characteristic α values for phenyl radical trapped by PBN. These peaks appeared in all ESR spectra obtained from sonicated solutions of 2-PCB ($n = 20$) and 4-PCB ($n = 19$) with irradiation times longer than 10 minutes (n = number of experiments).

Note that the integrated peak area (intensity) of the signal correlates with the spin adduct concentration, and is therefore proportional to the initial concentration of free radical in solution. At the highest power intensity (30.4 Wcm^{-2}), the peak intensity is highest. This indicates that the rate of formation of phenyl radical, and therefore, thermolytic cleavage of the biphenyl moiety, is accelerated at higher sound intensities. The enhancement can be understood by considering bubble implosion and the resulting conditions within the bubble. Acoustic intensity is directly related to acoustic pressure as described in Equation 1, which in turn determines the final temperatures and pressures within the bubble (Equations 2, 3).

$$I = \frac{P^2}{2\rho C} \quad (1)$$

$$T_{\max} = T_0 \frac{P_m(k-1)}{P_0} \quad (2)$$

$$P_{\max} = P_0 \left(\frac{P_m(k-1)}{P_0} \right)^{\left(\frac{k}{k-1} \right)} \quad (3)$$

where I = sound intensity, P = acoustic pressure, ρ = density of water, C = speed of sound in water. T_{\max} , P_{\max} = maximum temperature and pressure at implosion, T_0 = ambient temperature of water (22°C in our experiments), P_0 = pressure in bubble at its maximum size (assumed to be the vapor pressure of water), P_m = peak pressure of the bubble, which is the sum of the hydrostatic and acoustic pressure (P , from Eqn. 1), and k = polytropic index of saturating gas.

Thus, as the sound intensity increases, higher temperatures and pressures exist within the bubble interior, which then enhance the overall decomposition rate of the PCBs. In addition, the formation of organic free - radicals is also enhanced at higher sound intensities. These observations are consistent with previous reports of enhanced decomposition kinetics at higher acoustic intensities.

A second set of ESR experiments highlights the correlation between physico-chemical properties and sonolytic decomposition kinetics. **Fig. 2** is a comparison of the first derivative spectra for separate, sonicated solutions of 2-PCB (4.6 μM) and 4-PCB (5.4 μM). Both congeners yield phenyl radical. Note that after 10 minutes of sonication at 30.4 W cm^{-2} , the signal intensity was higher for 2-PCB than for 4-PCB despite the lower initial concentration of 2-PCB. Because the mole ratio of spin-trap (20 mM) was in such large excess compared to either congener, the trapping efficiency was most likely the same for each congener. Also, formation of the phenyl radical involves thermolysis of C-C bond, which can only occur within high temperature regions of the cavitation bubble (the bubble interior, or at the gas-liquid interface), and not within the bulk solution at ambient temperature. Therefore, a faster accumulation of phenyl radical is consistent with the hypothesis that a relatively greater number of 2-PCB ($\log H = -0.09$) molecules partition into the bubble interior compared to 4-PCB ($\log H = -0.63$).

Fig. 3 demonstrates the time variation of the PBN-phenyl spin-adduct accumulation during sonication of 2-PCB. The spin-adduct initially accumulates, corresponding to formation of phenyl radical from the destruction of 2-PCB. Eventually, the intensity of the peak decreases because the concentration of the parent compound, 2-PCB, has decreased, and therefore, the rate of formation of phenyl radical decreases. Also, the spin-adduct itself further reacts during sonolysis. The formation of phenyl radical confirms thermolytic cleavage of the biphenyl rings, which is a key step in PCB destruction. Additional reactions yield other by-products, which were identifiable by Gas Chromatography – Mass Spectroscopy (GC-MS).

Three groups of products were identified with the mass spectra of sonicated PCB solutions. The first group includes biphenyl and toluene, ethyl benzene, diethylbiphenyl, and dibutenylbiphenyl. The second group includes phenol, propylphenol, di-*tert*-butylphenol, and

cyclohexenyl di-phenol. Biphenyl was found only during the sonication of 54 μM 2-PCB, while others were detected as sonication products at lower initial concentration (5.2 μM) of 2-PCB. The third group consists of ethyl benzene, diethylbiphenyl, and trichlorophenol detected during the sonication of 2,4,5-PCB.

There are two possible pathways for formation of biphenyl. One is cleavage of C-Cl bond followed by $\text{H}\bullet$ addition:



Another pathway is combination of two phenyl radicals:



Bond energies can be used to estimate activation energies. Therefore, because the bond energy for $\text{Cl-C}_{12}\text{H}_9$ is lower (397 kJmol^{-1}) than that of $\text{C}_6\text{H}_5\text{-C}_6\text{H}_5\text{Cl}$ (418 kJmol^{-1}), dechlorination is expected to occur more rapidly than recombination of the biphenyl. The ESR data cannot be used to differentiate between these two pathways, however, because $\text{Cl}\bullet$ is difficult to detect directly by ESR, due to its high reactivity. The presence of methanol as a co-solvent contributes to the formation of $\text{CH}_3\bullet$ and $\bullet\text{CH}_2\text{OH}$ during sonication of 54 μM 2-PCB, but is unlikely to impact the formation of biphenyl.

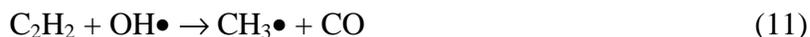
The following pathways are proposed for the formation of other compounds in the first group. The thermal degradation of phenyl radical can produce $\text{C}_6\text{H}_4\bullet$:



Alkyl fragments result from rupture of the aromatic ring. β -scission of phenyl radical will yield $n\text{-C}_4\text{H}_3\bullet$ and acetylene:



The acetylene then reacts with $\text{OH}\bullet$ to form methyl radicals and carbon monoxide:



The formation of group one compounds results from reactions between the phenyl radical and $\text{C}_6\text{H}_5\bullet$, $\text{C}_6\text{H}_4\bullet$, $\text{C}_4\text{H}_3\bullet$, $\text{CH}_3\bullet$, $\text{H}\bullet$ and C_2H_2 . Group two compounds are formed by direct attack of group one compounds by $\bullet\text{OH}$.

The third group of compounds (ethyl benzene, diethylbiphenyl, trichlorophenol) were detected during sonication of 2,4,5-PCB. Cleavage of the biphenyl ring yields a phenyl and a trichlorophenyl radical. Subsequent reaction of the phenyl radical with C_2H_2 will result in formation of ethyl benzene, and attack of the trichlorophenyl radical by $\bullet\text{OH}$ will yield trichlorophenol. The presence of hexane as a co-solvent can produce alkane free - radicals and may contribute to the formation of ethyl benzene and diethyl biphenyl. However, during sonication, C_2H_2 forms even in the absence of hexane. The wide range of organic by-products detected by GC/MS result from the reaction of aromatic free - radicals with other carbon centered radicals, or with hydroxyl radical ($\bullet\text{OH}$). These experimental results confirm that free radical attack and thermolysis are major mechanisms in sonochemistry.

b. Sonication of 1,4-Dioxane

1,4-Dioxane is a volatile organic compound suspected of being a human carcinogen and is resistant to degradation by aerobic and anaerobic biological processes. This research focuses on the novel use of sonolysis in environmental pollution control applications. The objectives of this investigation are to 1) examine the kinetics and mechanisms of 1,4-dioxane degradation

during sonolysis and 2) enhance the performance and efficiency of sonochemical technology. This current study considered the effects of various sparge gases (O₂, Ar, and air) at different sound frequencies for the degradation of 1,4-dioxane and examined the OH[·] production of ultrasound in order to determine the optimal conditions for contaminant mitigation.

The degradation of 1,4-dioxane is also shown to be more efficient with a pure oxygen sparge than with pure Ar (Fig. 4). Although the thermal conductivity of O₂ is higher than that of Ar (48.1 vs. 30.6 mW/m-K), the production of additional radical species with O₂ can compensate for the lower internal cavitation temperature that arises with O₂. However, it is clear that a combination of the sparge gases O₂ and Ar lead to higher degradation rates than either pure gas, with the highest degradation rate occurring at a 75% Ar/25% O₂ ratio ($k = 4.10 \times 10^{-4} \text{ s}^{-1}$).

With the 75% Ar/25% O₂ sparge ratio, there is an optimum balance created between the higher heat generated during acoustic cavitation from Ar and the generation of active radical species from O₂ which leads to the most effective conditions for compound destruction. The observed rate constant with a 75% Ar/ 25% O₂ sparge gas ratio is higher than that determined in the direct photolysis of 1,4-dioxane ($k = 6.4 \times 10^{-5} \text{ s}^{-1}$) but lower than the observed rate constant for the UV/H₂O₂ degradation of the same compound ($8.7 \times 10^{-3} \text{ s}^{-1}$).

The impact of frequency on sonolytic processes is significant. The results have varied widely due to the use of different types of ultrasonic emitters such as probes or plates and the diversity of reactors incorporated. The effect of sonolysis on the degradation rate of 1,4-dioxane was studied over a range of frequencies using the same transducer and reactor system for each experiment. The sparge gas ratio used was 75% Ar/25% O₂ and the results are shown in Figure 5. The fastest degradation rate occurs at a frequency of 358 kHz followed by 618, 1071, and 205 kHz.

The effect of sparging with air instead of argon or oxygen at different ultrasonic frequencies was considered and the results are shown in [Figure 6](#). Air has a thermal conductivity of 45.7 mW/m-K which is higher than Ar but lower than O₂. The rate constants observed in solutions saturated with pure air, Ar, and O₂ at 358 kHz are 1.23 x 10⁻⁴, 8.67 x 10⁻⁵, and 1.37 x 10⁻⁴ s⁻¹, respectively. The observed trends with air sparging are very similar to that of the 75% Ar/25% O₂ sparge with the two best degradation rates occurring at 358 kHz and 618 kHz. The kinetic rates, however, are lower by a factor of three in the air sparged solutions at each corresponding frequency when compared to the optimal combined Ar/O₂ sparge.

A number of experiments need to be performed in order to fully understand the mechanisms of 1,4-dioxane degradation. A thorough analysis of 1,4-dioxane byproducts will be evaluated using various analytical instruments.

c. Impact of Solid Particles on Sonolytic Destruction of Halogenated Hydrocarbons

Most investigations of sonochemistry for the purposes of water pollution control are performed with reagent grade water, which does not closely mimic environmental matrices. Natural waters and most industrial process streams contain solid impurities. Therefore, it is necessary to assess the viability of sonication in heterogeneous systems.

Previous investigations of heterogeneous sonochemistry have involved ultrasonic extraction of pollutants from sediments and ultrasound assisted reactions employing solid catalysts. However, more extensive quantitative results are needed concerning sonochemistry in environmentally relevant systems. We report results of a preliminary set of experiments, involving the ultrasonic irradiation of bromobenzene, trichloroacetonitrile, and chloropicrin in the presence of silica solids (15 μm and 10 nm).

The data in Fig. 7 demonstrate that in the presence of 15 micron solid particles, there is a slight or moderate impact on destruction kinetics. The destruction rate constant of trichloroacetonitrile (TCA) decreases by approximately 10% when the silica particle concentration is increased from 0 to 100 g L⁻¹. In the presence of 10 nm silica (Fig. 8), the trends are similar, with slight to moderate decreases in the reaction rate constant as the silica particle concentration increases.

In addition to adsorption, a number of other physical processes can occur in the presence of particles during sonication. For example, particles may serve as nucleation sites for cavitation bubbles. Further experimental work is required in order to adequately interpret these results.

Planned Activities

Further investigations of chemical kinetics and transformation products will be carried out during the final phase of the project. In order to truly understand sonochemical effects, the behavior of the individual bubbles and the bubble clouds must be more finely resolved. Physical characterization of cavitation bubble clouds will also be performed. Thus, a more fundamental link will be established between bulk, observable parameters and sonochemistry, via the physics and hydrodynamics of the cavitating cloud.

Publications Resulting from This Work

Pfalzer, U. and Hua, I.; Ultrasonic Irradiation of Carbofuran: Decomposition Kinetics and Reactor Characterization, *submitted*, October, 1998 to *Journal American Water Works Association*.

Zhang, G. and Hua, I.; Cavitation Chemistry of Polychlorinated Biphenyls: Detection of Reactive Intermediates and By-Products and the Impact of Ultrasonic Frequency, *submitted*, October, 1998 to *Environmental Science and Technology*.

Schramm, J. and Hua, I.; Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism and Mass Balances, *submitted*, November, 1998, to *Environmental Science and Technology*.

Conference Presentations Resulting from This Work

"Degradation of Dichlorvos by Sonolysis", Jennifer Schramm and Inez Hua at American Chemical Society Meeting; September, 1997, Las Vegas, NV.

"Sonochemical Degradation of Carbofuran in a Parallel-Plate Near-Field Acoustical Processor", Ulrike Pfalzer and Inez Hua, 20th Annual Midwest Environmental Chemistry Workshop, November 9, 1997, Indiana University, Bloomington, IN.

"Destruction of Polychlorinated Biphenyls in Acoustically Cavitating Systems", Guangming Zhang and Inez Hua, at American Chemical Society Meeting, March 1998, Dallas, TX.

Inez Hua, "The Use of Ultrasonic Irradiation in Environmental Engineering Processes", at Borchardt Conference, February, 1999, The University of Michigan, Ann Arbor, Michigan.

Other Access To Information

Hua, I., Höchemer, R.H., Hoffmann, M. R., Sonolytic Hydrolysis of *p*-Nitrophenylacetate: The Role of Supercritical Water, *Journal of Physical Chemistry*, 1995, 99(8), pp. 2335-2342.

Hua, I., Höchemer, R.H., Hoffmann, M. R., The Sonochemical Degradation of *p*-Nitrophenol in a Parallel-Plate Near-Field Acoustical Processor, *Environmental Science and Technology*, 1995, 29(11), pp. 2790-2796.

Hua, I., Hoffmann, M. R., Kinetics and Mechanism of the Sonolytic Degradation of CCl₄: Intermediates and By-Products, *Environmental Science and Technology*, 1996, 30(3), pp. 864-871.

Hoffmann, M. R.; Hua, I.; Hoechemer, R., Application of Ultrasonic Irradiation for the Degradation of Chemical Contaminants in Water, *Ultrasonics Sonochemistry*, 3(3), pp. S163-S172, 1996.

Weavers, L. K., Hua, I., Hoffmann, M. R., A New Advanced Oxidation Process: Photoassisted Oxidation of Triethanolamine by Periodate, *Water Environment Research*, 69(6), pp. 1112-1119, 1997.

Hua, I., Hoffmann, M. R., Sonochemical Production of Hydroxyl Radical and Hydrogen Peroxide: The Effect of Frequency and Saturating Gas,*Environmental Science and Technology*, 31(8), pp. 2237-2243, 1997.

Hoffmann, M. R., Hua, I., Höchemer, R. H., Willberg, D., Lang, P., Kratel, A., chapter entitled “**Chemistry under Extreme Conditions in Water Induced by Electrohydraulic Cavitation and Pulsed-Plasma Discharges**”, in *Chemistry Under Extreme or Non-Classical Conditions*, pp. 429-478, edited by R. Van Eldik and C. D. Hubbards, New York: Wiley ; Heidelberg : Spektrum, 1997.

Professor Hua's Web URL is: http://CE.www.ecn.purdue.edu/CE/Fac_Staff/FACULTY/hua

Figures

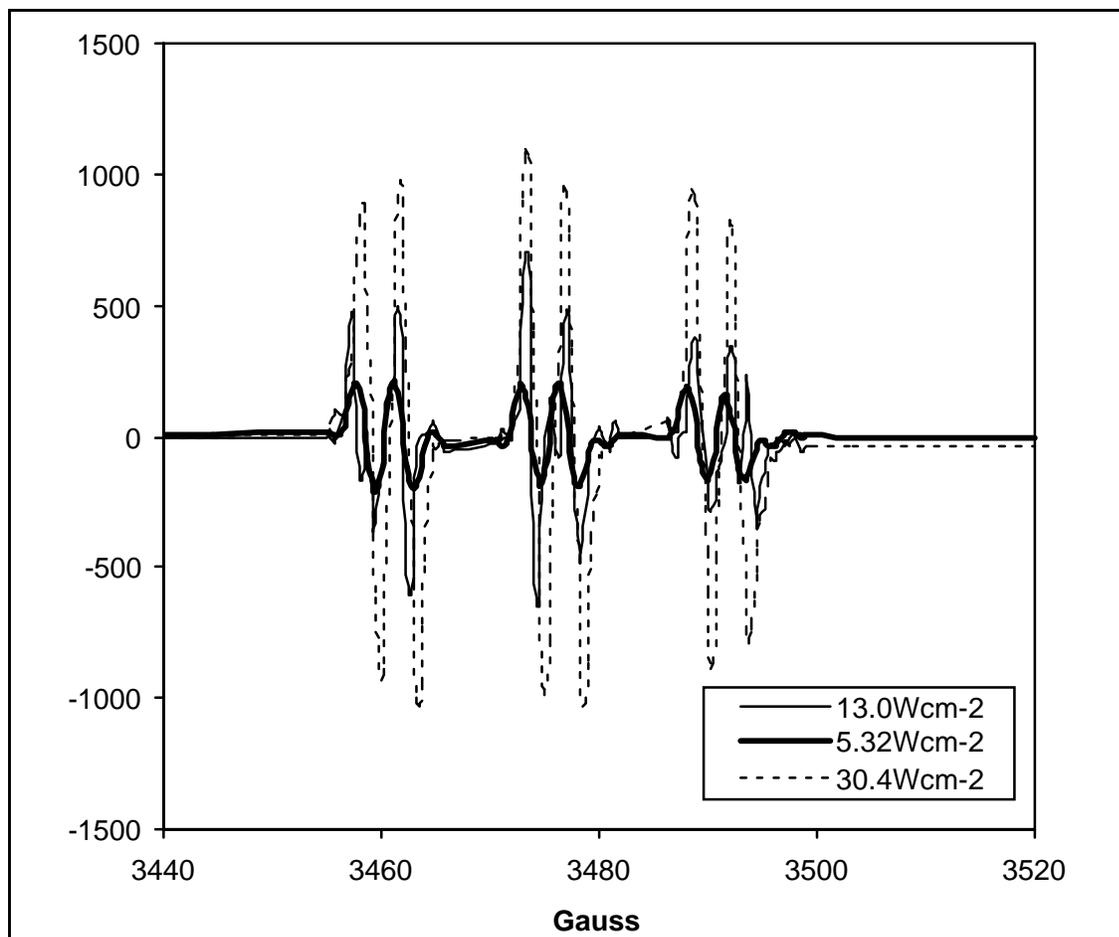


Fig. 1: First - derivative ESR spectrum indicating the accumulation of PBN-phenyl after 10 minutes of sonicating an Ar-saturated solution of 2-PCB (4.6 μM) at 20 kHz and varying sound intensities.

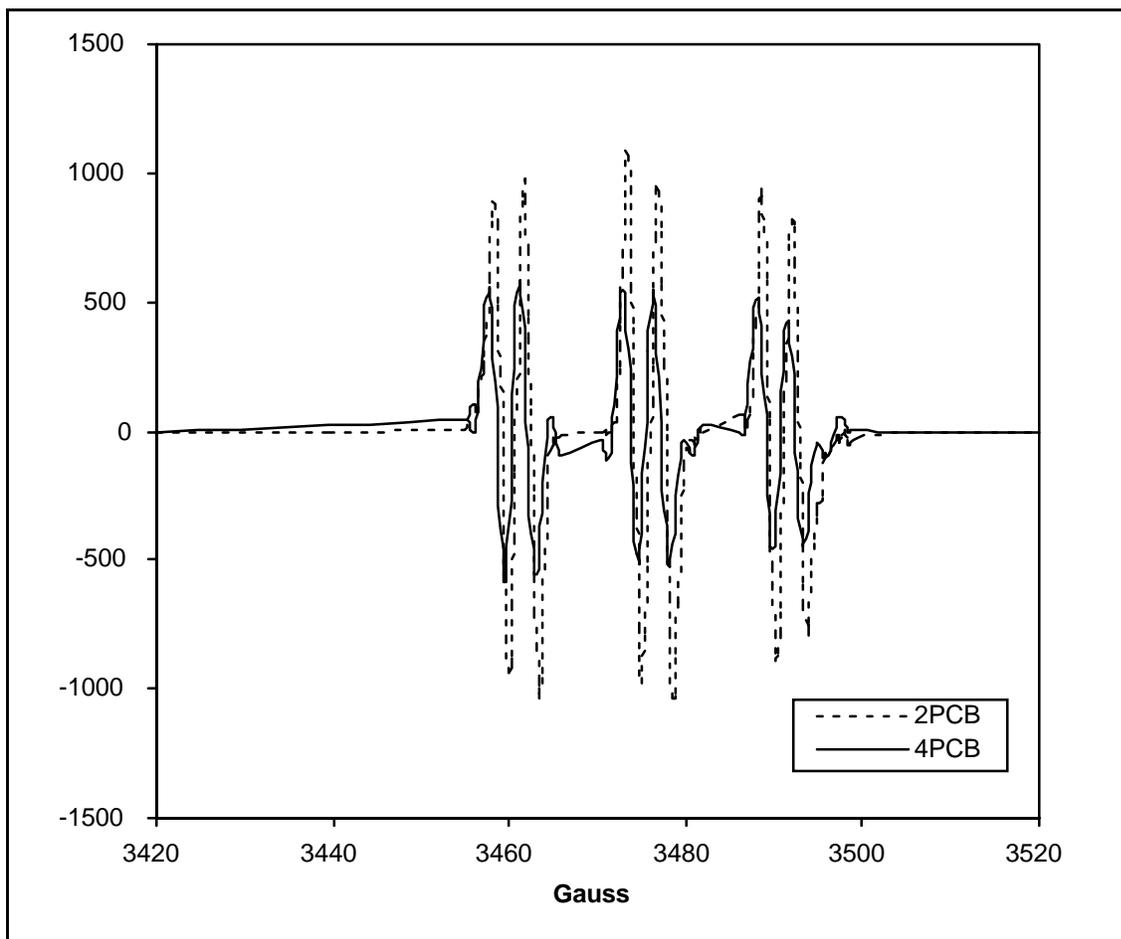


Fig. 2: First – derivative ESR spectrum of PBN-phenyl detected after 10 minutes of sonicating separate solutions of 2-PCB ($4.6 \mu\text{M}$) or 4-PCB ($5.2 \mu\text{M}$) at 20 kHz and 30.4 Wcm^{-2} in an Ar - saturated solution.

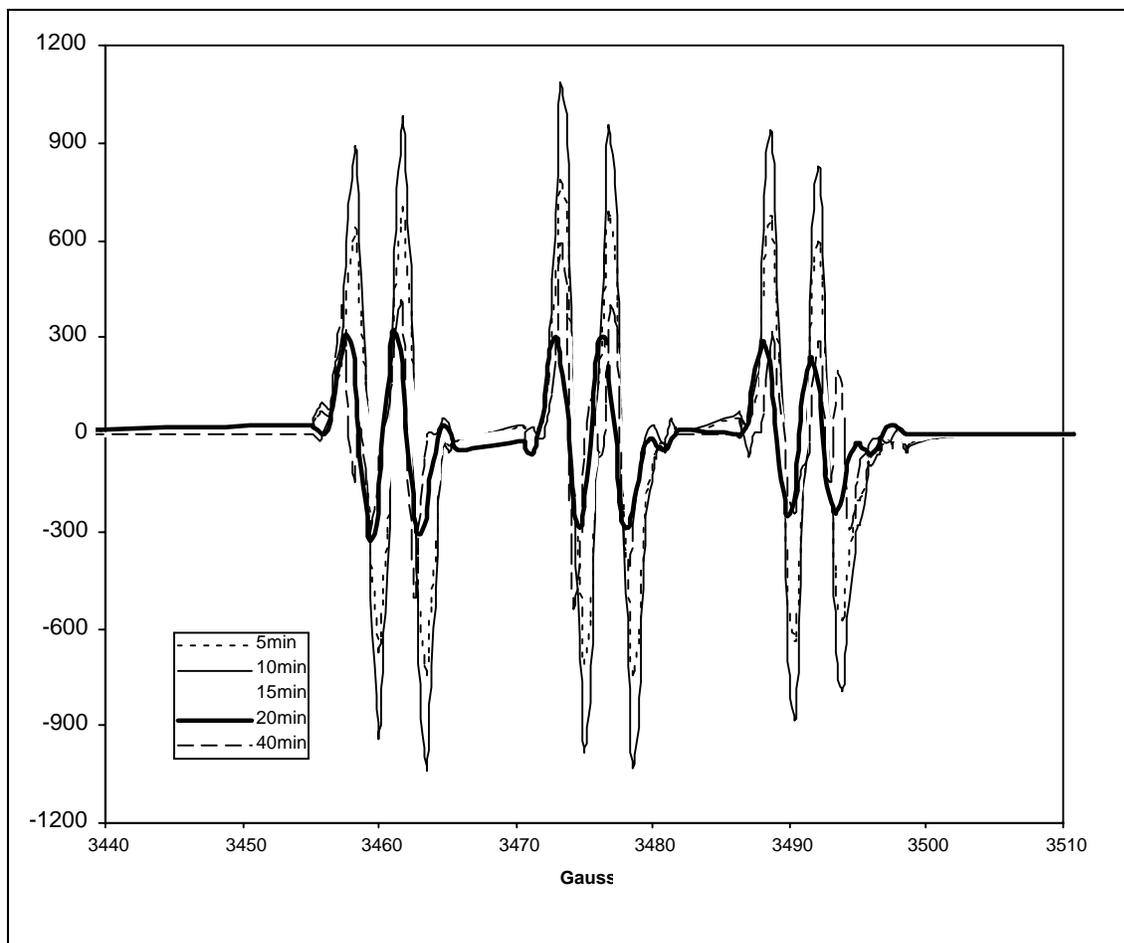


Fig. 3: First – derivative ESR spectrum indicating the accumulation of PBN-phenyl during sonication of 2-PCB ($4.6 \mu\text{M}$) at 20 kHz and 30.4 Wcm^{-2} in an Ar saturated solution. A maximum peak area occurs after 10 minutes of sonication.

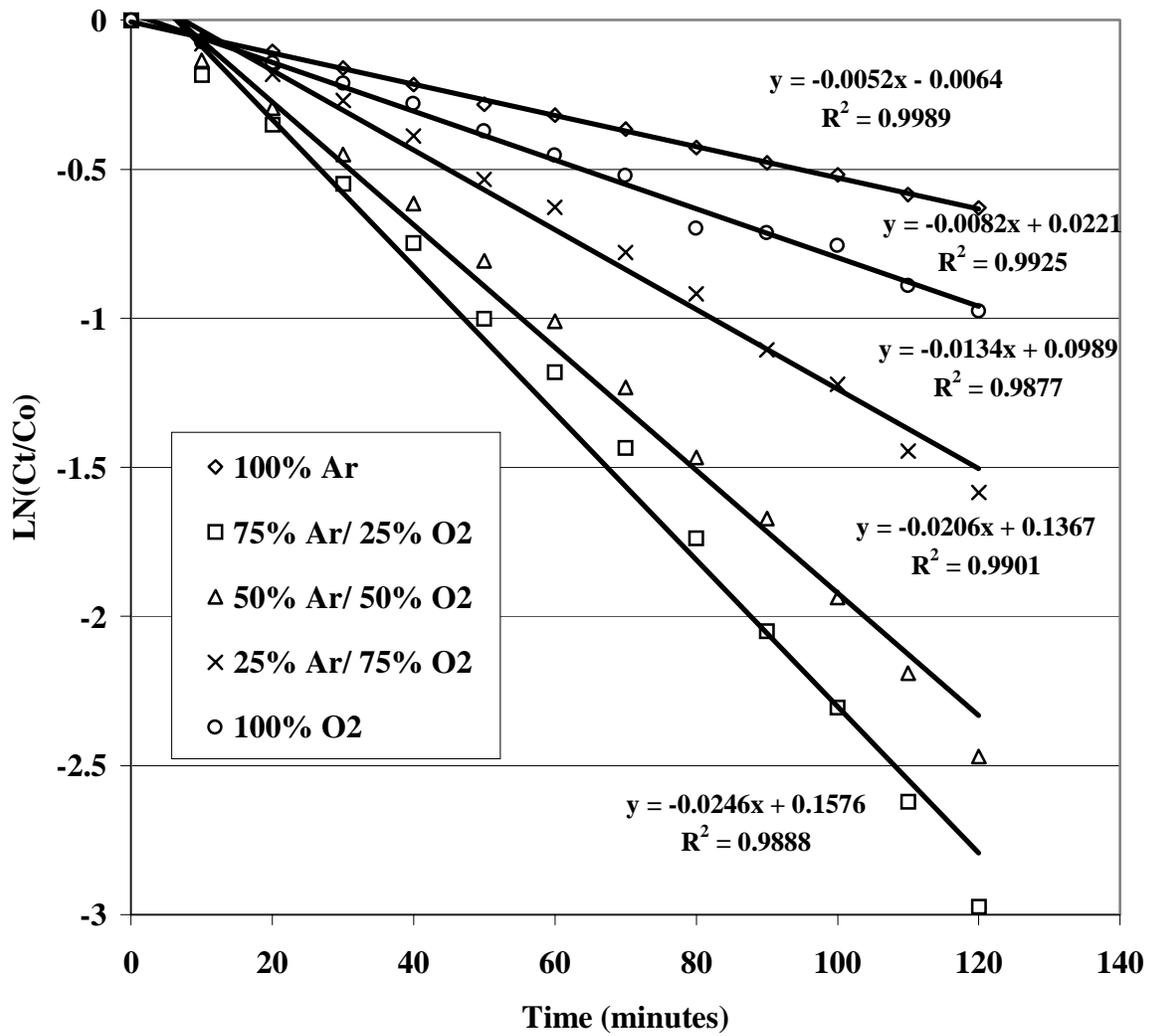


Figure 4: 1,4 - Dioxane degradation with various gas spargers. Frequency = 358 kHz and initial 1,4 - Dioxane concentration = $C_0 = 1$ mM. C_t = 1,4 - Dioxane concentration at time, t.

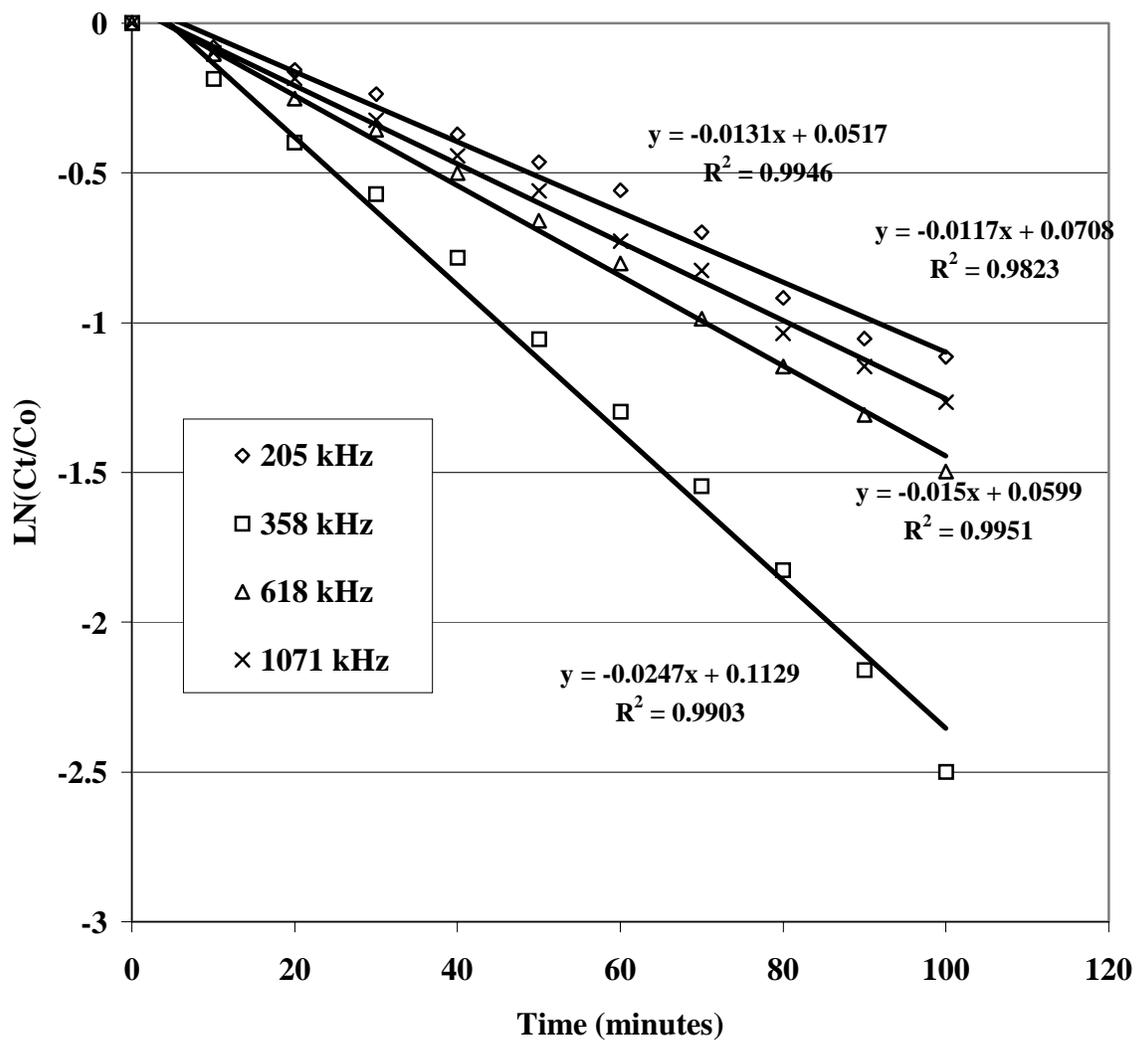


Figure 5: 1,4 dioxane degradation at four ultrasonic frequencies using the glass reactor : sparge gas = 75% Ar/25% O₂. C_t = 1,4 – Dioxane concentration at time, t, and Co = initial 1,4 – Dioxane concentration.

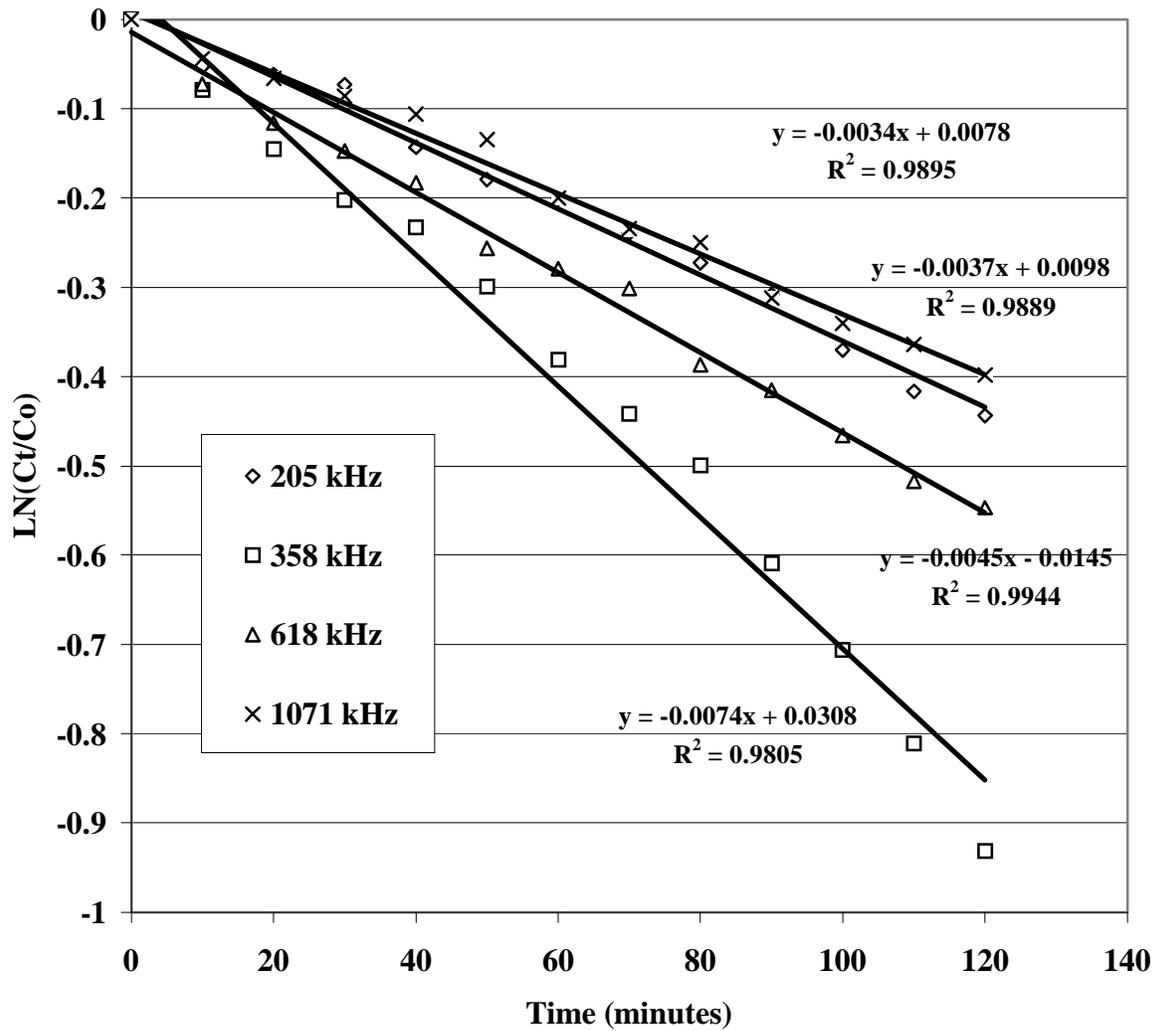


Figure 6: 1,4 Dioxane degradation at four ultrasonic frequencies using the glass reactor: sparge gas = 100% air. C_t = 1,4 – Dioxane concentration at time, t, and C_0 = initial 1,4 – Dioxane concentration.

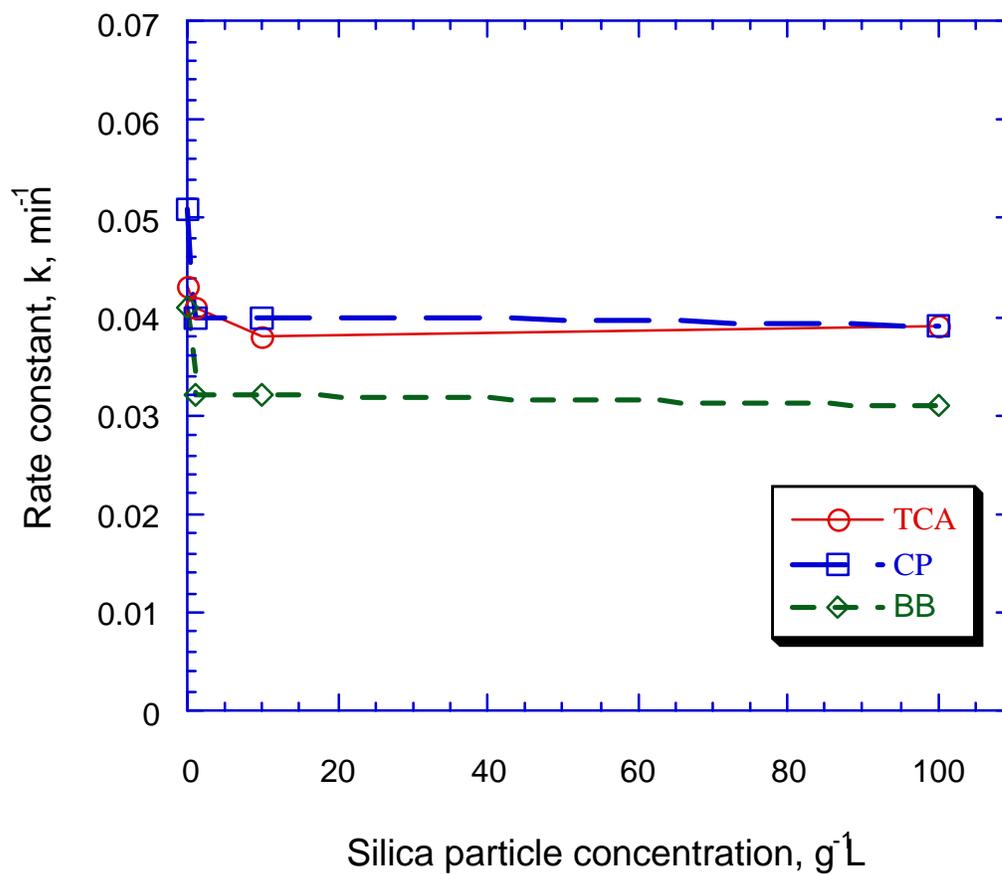


Figure 7: Sonication of trichloroacetonitrile (TCA), chloropicrin (CP), and bromobenzene (BB) in air-saturated solutions and intensity = 30.8 W cm^{-2} . 15 micron silica particles were employed.

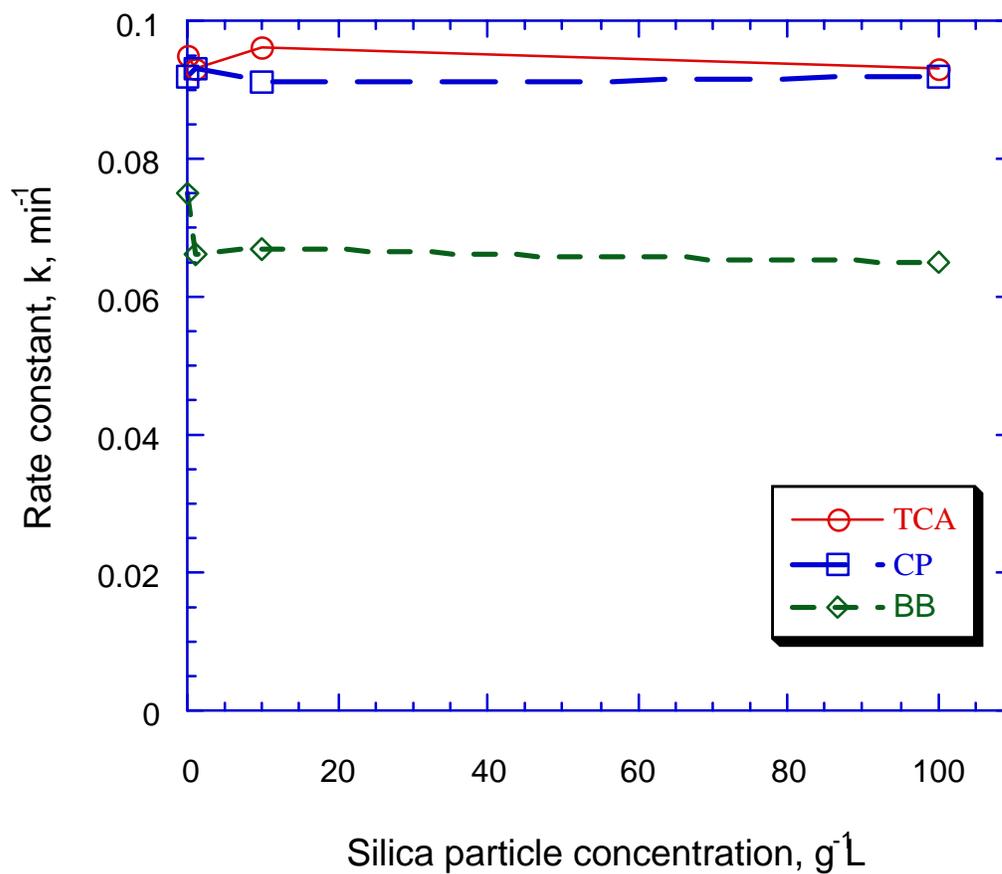


Figure 8: Sonication of trichloroacetonitrile (TCA), chloropicrin (CP), and bromobenzene (BB) in air-saturated solutions and intensity = 66.2 W cm^{-2} . 10 nm silica particles were employed.