Conf-911133--8

ULTRASONIC PROCESS FOR DETOXIFICATION OF GROUNDWATER

BY

ANL/CP--73172

DE92 004142

Jiann M. Wu, H.S. Huang, C.D. Livengood

Energy Systems Division

Argonne National Laboratory

Argonne, Illinois 60439

Prepared for Presentation at

AIChE National Meeting

Los Angeles, California, November, 1991

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ULTRASONIC PROCESS FOR DETOXIFICATION OF GROUNDWATER

Introduction

Chemical ultrasonics began in 1927 when Richards and Loomis reported the acceleration of conventional reactions and the redox process by ultrasound (1). Since then, a number of chemical reactions have been observed in an ultrasonic field (2-4). In recent years, attention has focused upon the application of ultrasonic energy to water pollution, especially in removing toxic and hazardous organic compounds from contaminated water (5). Removal of these compounds may be difficult and costly if very low concentration levels must be achieved. Conventional methods have included packed-bed aeration and activated carbon adsorption. However, aeration is useful for only volatile compounds, and adsorption is ineffective with some types of organic materials. In addition, both techniques are non-destructive and require disposal or further treatment of the organic materials. By contrast, the ultrasonic process has the advantage of completely destroying or converting these organics, and not simply transferring them to another medium.

The chemical effects of ultrasound are due to the phenomenon of acoustic cavitation (6). Sound is transmitted through any fluid as a wave consisting of alternating compression and rarefaction cycles. If the rarefaction wave is sufficiently powerful, it can develop a negative pressure large enough to overcome the intermolecular forces binding the fluid. As a

result, the molecules are torn apart from each other and form tiny microbubbles. These microbubbles gradually grow during the compression/rarefaction cycles until they reach a critical size. Subsequent compression then causes the microbubbles to collapse almost instantaneously, thereby releasing a large amount of energy. Temperatures of the order of 5000 K have been experimentally obtained (7), and pressures of the order of 1000 atmospheres have been calculated (8).

The primary chemical reactions result, therefore, from the transient state of these high pressures and temperatures, both during and immediately after collapse of the microbubbles (9,10). Solvent and solute vapors in the cavity undergo direct thermal dissociation to yield CO_2, H_2O, and radicals, such as hydroxyl and atomic hydrogen. Some of these radicals may recombine to form new compounds. In the bulk liquid phase, secondary reactions between solute molecules and radicals generated in the cavities also take place. These two reaction schemes together are responsible for the total chemical effect of ultrasonics upon the solution.

In this paper, we present the results of an investigation of the ultrasonic irradiation of carbon tetrachloride at various pH values, temperatures, and power intensities. Kinetic data and selected chemical mechanisms are discussed and proposed. To study oxidant efficiency, chemical oxidants, such as hydrogen peroxide, are also considered. This work is part of a project entitled "Ultrasonic Process for Detoxification of Groundwater and Soil",

sponsored by the U. S. Department of Energy, Office of Technology Development, to develop an innovative process for the effective destruction of chlorinated organics in soil and groundwater.

Experimental Considerations

Reaction Apparatus

Irradiations were carried out with an ultrasonic power supply (Sonics & Materials, VC 600) with a continuously variable output from 0 to 600 W, operating at 20 kHz. Figure 1 shows the schematic diagram of the experimental apparatus, and Figure 2 shows a close-up of the reaction cell. The ultrasonic intensity at the titanium tip of the sonication probe was about 27 W/cm^2. The sonication vessel was a borosilicate glass cell with a stainless steel collar, which could be screwed onto the horn of the ultrasonic probe so that the probe was immersed in the sample solution as sonication proceeded. The reaction vessel had side arms so that the oxidant, such as the hydrogen peroxide, could be introduced into the reactor, and gas samples could be directed to a gas analysis system.

The temperature inside the reaction vessel was kept relatively constant by circulating the cooling water in a constant-temperature bath, which was continuously monitored by means of a thermocouple probe and temperature readout. An alternative ultrasonic power supply (Sonics & Materials, VC 60) was used to study the effect of power intensity upon the destruction of organics. The major improvement of this apparatus

is the addition of a wattmeter, which displays the actual, instantaneous ultrasonic power delivered into the sample solution. In this way, converter and probe losses can be automatically deducted so that the effect of power intensity can be accurately investigated.

Materials

Carbon tetrachloride (CCl_4), sulfuric acid (certified ACS grade, Mallinckrodt, Inc.), hydrogen peroxide (30%, analytical grade, Mallinckrodt, Inc.) and n-hexane (certified for trace environmental analysis by capillary GC & GC-MS, Bardick & Jackson) were used as received by the suppliers. Sodium sulfate (certified ACS grade, Mallinckrodt, Inc.) was washed by n-hexane to remove trace impurities and was dried in an oven (104 °C) overnight before using. A standard CCl_4 solution was prepared by stirring the neat liquid with laboratory deionized water overnight and was equilibrated for at least 24 hours. This standard solution was then used to prepare all of the sample solutions for the subsequent experiments.

Analytical Method

Analysis of CCl_4 was carried out by a gas chromatograph equipped with an electron capture detector. A glass column packed with a 80/120 Carbopack B/3%, SP-1500 stabilizer was used after it had been conditioned at 230 °C for more than 15 hours. Immediately following the experiment, irradiated sample solutions were extracted with n-hexane and were dehydrated by sodium sulfate before being analyzed. The pH value of the sample

solution in the pH-effect study was determined by using a Cole-Parmer Chemcadet pH/ion/mv meter (model 5986-50), which was calibrated with standard solutions of pH 4, 7, and 10 before use.

Experimental Procedures

A 15-mL sample solution, which was diluted from the standard CCl_4 solution, was prepared for each experiment and was irradiated for a desired length of time. The power intensity delivered into the solution was regulated by a controller on the power supply panel. The temperature inside the reactor was monitored continuously throughout the experiment. After sonication ceased, the irradiated solution was extracted, dehydrated, and then stored in a Teflon-sealed sampling bottle for future treatment or analysis.

Chemical Kinetic Mechanism and Model Development

The chemical mechanism presented in Table 1 was developed by systematically considering the major plausible elementary reactions of water, dissolved air (nitrogen and oxygen), organics (CCl_4), and their related reactions in the field of ultrasonics (11-13). The reactions are initiated by the dissociation of water molecules in the cavitation holes (Eq. 1). Atomic hydrogen (H) and hydroxyl radicals (OH) are formed through this reaction. These two radicals recombine to form water or hydrogen molecules (H_2), or to react with oxygen molecules (O_2) to yield hydroperoxide radicals (HO_2) and hydrogen peroxide (H_2O_2) (Eqs. 2 to 6). These radicals further react with the H_2O_2 produced in

these reactions to form H_2 molecules, water, and other radicals (Eqs. 7 to 10). In order to simplify the treatment, we will not consider here the secondary reactions of H and OH with the H_2O_2 that is formed in the system.

In the presence of dissolved nitrogen, nitrogen molecules (N_2) decompose in the cavitation holes (Eq. 11) to form atomic nitrogen (N). Following a series of reactions, N then reacts with the OH radicals produced from the dissociation of water and related reactions to yield nitrate and nitrite (Eqs. 12 to 15). Atomic nitrogen also reacts with H and O_2 molecules to regenerate N_2 and H_2 molecules and to produce nitro-oxide (NO) and O_2 radicals (Eqs. 16 to 18).

Oxygen molecules dissolved in the water also decompose in the cavitation holes (Eq. 19) to produce atomic oxygen (O) and compete with Eq. 2, leading to the formation of hydroxyl radicals (Eq. 20). Atomic oxygen then reacts with H_2 molecules, H_2O_2, and HO_2 to form O_2 molecules and other radicals, such as H and OH (Eqs. 21 to 23).

The target contaminant, CCl_4, present in the water is either directly decomposed in the cavities (Eq. 28) or oxidized by radicals (Eqs. 24 to 27). If the reaction does not proceed to completion, the final products of the irradiation of CCl_4 by ultrasound are water, carbon dioxide, and/or some other chemical compounds.

Based on the chemical kinetic mechanism proposed above, the primary reaction pathway appears to be the thermal dissociation

in the cavities, such as those represented in Eqs. 1, 11, 19, and 24. The high temperature and pressure in the cavitation bubbles provide the activation energy required for the bond cleavage. Water, nitrogen, oxygen, and carbon tetrachloride molecules decompose in these cavities to directly form the radicals. These radicals then either react with each other to form new molecules and radicals or diffuse into the bulk liquid to serve as oxidants. The secondary reaction seems to be in the bulk-liquid phase, where CCl_4 and other molecules are oxidized by oxidants, such as the H and OH radicals generated in the bubbles.

Therefore, to better clarify these reactions, the whole system can be divided into two major areas: (1) the cavitation bubbles, in which temperature and pressure are extremely high and in which molecule vapors in the bubbles reach supercritical conditions and decompose; and (2) the bulk-liquid phase under normal operating temperatures and pressures, in which molecules are oxidized by radicals to form new products. In a batch reactor with reactions undergoing the bulk-liquid phase, we assume a second-order rate constant, in which the destruction rate of CCl_4 can be represented by the following equation:

$$-d[CCl_4] / dt = k_{liquid} = k_{24}[OH][CCl_4] + k_{25}[H][CCl_4] + k_{26}[HO_2][CCl_4] + k_{27}[O][CCl_4]$$

which is the general second-order reaction rate formula. The total disappearing rate of CCl_4 equals the accumulated rate of

all of the related reactions in the mechanism. If the reaction takes place in the cavitation bubbles, it is reasonable to assume a second-order rate constant again. In this case, the destruction rate of CCl_4 can also be expressed by a similar rate formula:

$$-d[CCl_4] / dt = k_{bubble} = k_c * k_{28}[CCl_4][M]$$

where M is any collision partner and k_c is the system adjustment coefficient, which is a function of bubble concentration, bubble radius, mixing extent of the system, etc. This coefficient is assumed to be a constant if all of the experimental conditions, such as reaction vessel size, steady-state temperature, and power intensity, are unchanged. This coefficient can be obtained by a best fit of the experimental data into the model. Because the reaction occurs in the cavity, $[CCl_4]$ in the k_{bubble} formula represents the concentration of CCl_4 in the vapor phase. If we assume an ideal gas and Rault's law to hold, this value can be calculated by Henry's law.

Hence, in addition to CCl_4, the net reaction rates for all the other compounds in the system can also be expressed in similar rate formulas, or differential equations, that describe the decreasing or increasing rates in the field of ultrasonics. If all of the reaction rate constants are available, these differential equations could be solved simultaneously to obtain the individual concentration profile for each species as a function of irradiation time.

Results and Discussion

Exposure of CCl_4 solutions to ultrasound in the presence of dissolved air results in a decrease of the $[CCl_4]$ in the solutions. Greater than 99% removal efficiency was obtained in the current experiment. Figures 3, 4, and 5 show the plot of $[CCl_4]$ versus sonication time at various initial $[CCl_4]$. Initial $[CCl_4]$ as high as 130 ppm (Figure 3) dropped to about 5 ppm after 6 minutes of irradiation, while initial $[CCl_4]$ of 1.6 ppm (Figure 5) dropped to about 0.05 ppm at the same irradiation time. The concentration of residual CCl_4 decreased exponentially with sonication time. With higher initial $[CCl_4]$ within the same sonication period, greater decreases in residual CCl_4 were observed; however, the destruction efficiency was about the same. First-order plots of $\ln[CCl_4]$ versus sonication time for various initial $[CCl_4]$ are shown in Figure 6. The ultrasonic degradation of $[CCl_4]$ apparently followed first-order kinetics within the current experimental concentration range. An average first-order rate constant of $k=0.7\ min^{-1}$ was determined from the slopes of these plots. It has been reported (14) that at low $[CCl_4]$, CCl_4 destruction should follow a first-order reaction, but at higher concentrations this should become a zero-order reaction.

Temperature control in the reaction vessel is an important factor in maintaining a high destruction rate of CCl_4 in the solution. In sonochemistry, it has been reported (6) that one should not attempt reactions in a solvent (here, water) that is near its boiling point (100 °C), because the rarefaction cycle

causes the water to boil, as a result of the reduced pressure generated; consequently, any cavitation bubbles formed will fill with water vapor almost instantaneously. This water vapor could reduce the extremes of temperature and pressure generated and thus decrease the direct destruction efficiency of the organics. On the other hand, the secondary reactions occurring in the liquid phase may be enhanced by operating the system at higher temperatures.

The effect of a steady-state temperature on the destruction efficiency of CCl_4 is shown in Figure 7. About 80% removal efficiency was observed for 4 minutes of irradiation; removal efficiency remained unchanged within a temperature range of 20 to 60 °C. These results illustrate that, with the temperature within this range, increasing the steady-state temperature of the irradiation solutions seems to have little effect on the CCl_4 destruction efficiency. In other words, manipulating the system at the optimum temperature range allows high removal efficiencies within reasonable operation times.

Ultrasonic power intensity is also an important factor affecting the CCl_4 destruction rate. In general, any increase in intensity will increase the sonochemical effect (15). However, it must be realized that intensity cannot be increased indefinitely (16,17). With an increase in power intensity, the bubbles may grow so large during rarefaction that the time available for their collapse is insufficient, and hence, the effective coupling of the ultrasonic energy to the system is reduced (6).

Figure 8 shows the effect of power intensity upon the destruction of CCl_4. After 1 minute of irradiation, the residual [CCl_4] decreases with the increasing power intensity. More CCl_4 molecules are destroyed at higher power intensities. The CCl_4 destruction rate versus power intensity is shown in Figure 9. Within the current experimental range, the destruction rate seems to have a linear relationship to the power intensity. Although threshold intensity was not determined, it is estimated to be lower than the 0.95 W/cm^2 shown on this figure. The destruction rate is negligible if the power delivered into the solution is lower than the threshold intensity.

The relationship between initial pH value and CCl_4 destruction is shown in Figure 10. Residual [CCl_4] decreases with increasing pH value between pH 3 to pH 9 within the same sonication period. Better sonication efficiency was observed at higher initial pH values; however, such improvement increasingly diminishes as the pH is raised above 6. Since most of the irradiations were conducted at near neutral conditions for groundwater treatment, the initial pH value seems to have a minimal effect upon CCl_4 removal.

Modeling of ultrasonic chemical kinetics was also carried out, based on the proposed mechanism described above. Assuming second-order reactions, all the reaction rate constants in the model can be obtained either from published data (reactions 1 to 27 (18-21)) or from experiments (reaction 28). Once determined, these constants are unchangeable and cannot be used as variables.

Therefore, no adjustable parameters are included in the model. Reverse reactions were not considered significant because no other chemicals have been added so far and because the concentrations of the products for each reaction were assumed to be much less than those of the reactants.

All of the elementary reactions proposed in the mechanism were transformed into a set of differential equations that describes the time variance of species concentrations based on the rate formulas k_{liquid} and k_{bubble}, depending on whether these reactions take place in the bulk-liquid phase or in the cavitation bubbles. The k_c value in the k_{bubble} equation was obtained by a best fit of the experimental data to the model, which was determined to be $2.5 * 10^{-11}$ for the system. With the initial concentration specified, these equations can be solved readily. Calculated results showed that the model fits the experimental data relatively well at low $[CCl_4]$ (below 10 ppm). Correlation coefficients greater than 0.99 were obtained. However, deviations were observed at higher $[CCl_4]$ (46.7 ppm). The predicted destruction rate was greater than that of the experiment. This might be because the organic vapor pressure in the bubble increases with increasing $[CCl_4]$ and, hence, Henry's law no longer applies at this high concentration. In these cases, the activity for each compound in the bubble may need to be taken into consideration.

The sensitivity of each reaction in the model was also tested. Results reveal that dissolved nitrogen concentration in

the system has a minimal effect upon the CCl_4 destruction rate, an effect that is neglected. The major reactions affecting the CCl_4 destruction rate were found to be the dissociation of water molecules and the decomposition of CCl_4 molecules in the bubble. In the bulk-liquid phase, the reaction between OH radicals and CCl_4 was predominant, followed by the reactions of the atomic hydrogen, atomic oxygen, and finally HO_2 radicals.

Hydrogen peroxide (H_2O_2), used as an oxidant, was added to the sample solution to study the effect of oxidant in the field of ultrasonics. With sonication, H_2O_2 is known to decompose in the cavitation bubbles to yield OH radicals. These radicals diffuse into the bulk liquid and increase the radical concentrations in the solution, thus enhancing the destruction rate of organics.

Figure 11 shows the CCl_4 destruction versus H_2O_2 dosages (as $[H_2O_2]/[CCl_4]$ ratio), with 2 minutes of irradiation. Initial $[CCl_4]$ as high as 6.5 ppm was reduced to around 0.9 ppm without adding any oxidant and was slowly reduced to about 0.7 ppm as the H_2O_2 dosage increased to 20:1. This decreasing amount is insignificant when compared with the addition of H_2O_2 dosages.

Figure 12 shows CCl_4 destruction versus time with the addition of only H_2O_2, without ultrasonics. Only slightly decreasing amounts of $[CCl_4]$ were observed after 60 minutes reaction time, and the effect was negligible.

These results illustrate that the addition of the H_2O_2 oxidant has almost no effect upon the CCl_4 destruction rate, both

with and without ultrasonics. This can be explained by comparing the CCl_4 reaction rate constants between the bulk-liquid phase (less than 10^7 min^{-1}) and the cavitation bubble (around 10^{12} min^{-1}). The CCl_4 is relatively inactive to radicals because all of the four free electrons are captured by chloride ions and form only single bonds (C-Cl) in the molecule. However, the single bond between C and Cl provides low dissociation energy (only about 80 kcal/mole), thus making it easier for the bonds to cleave in the cavitation bubbles. Therefore, the bulk-liquid reaction rate constant for CCl_4 is about five orders of magnitude smaller than that in the cavities. This difference makes the reactions in the cavitation bubbles predominant, and, hence, the addition of oxidants has only a minimal effect upon the whole system.

Conclusions

This study demonstrates that the ultrasonic process is a promising and effective method for the destruction of low concentrations of chlorinated organic compounds such as CCl_4 in water. Removal efficiencies of greater than 99% were achieved through this process. For the treatment of water containing CCl_4, the major reactions may be the bond-cleavage of water and of CCl_4 in the bubble. Under the current experimental conditions, physical operating conditions, such as steady-state temperature and pH value of the irradiated solution, were found to have little effect upon the CCl_4 destruction rate. However,

the CCl_4 destruction rate was found to be significantly affected by the intensity of the ultrasonic energy, with the destruction rate increasing proportionally to the intensity. By contrast, adding hydrogen peroxide as an oxidant has only a negligible effect upon the destruction rate, with or without ultrasonic irradiation.

Finally, mathematical modeling of ultrasonic chemical kinetics via a series of elementary reactions appears to be both a possible and valuable predictive tool for further exploring the means to control the complex ultrasonic process for the detoxification of groundwater.

Acknowledgment

This work was supported by the U. S. Department of Energy, Director of the Environmental Restoration and Waste Management, Office of Technology Development, under contract W-31-109-Eng-38.

References:

1. Richards, W. T.; Loomis, A. L., J. Am. Chem. Soc., 49, 3086(1927).
2. Suslick, K. S., Science, 247, 1439(1990).
3. Mason, T. J.; Lorimer, J. P., "Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry", John Wiley & Sons, New York, 1988.
4. Weissler, A.; Cooper, H. W.; Snyder, S., J. Am. Chem. Soc., 72,1976(1950).
5. Agranonik, Ya. R.; Karpukhin, V. F.; Fayngold, Z. L., Antibiotiki i Khimioterapiya, Russ., 35, 48-51(1986).
6. Mason, T. J., "Chemistry with Ultrasound", published for the Society of Chemical Industry, Elsevier Science Publishers Ltd, England, 1990.
7. Suslick, K. S.; Hammerton, D. A.; Cline, D. E., Jr., J. Am. Chem. Soc., 108, 5614(1986).
8. Shutilov, V. A., "Fundamental Physics of Ultrasound", Gordon & Breach Science Publishers, New York, 1988.
9. Kotronarou, A; Mills, G.; Hoffmann, M. R., J. Phys. Chem., 95, 3630-3638(1991).
10. Fitzgerald, M. E.; Griffing, V.; Sullivan, J., J. Chem. Phys., 25, 926(1956).
11. Margulis, M. A.; Didenko, Yu. T., Russian J. of Phys. Chem., 58(6), 848(1984).
12. Glaze, W. H.; Kang, J., Ind. Eng. Chem. Res., 28, 1573-1580(1989).

13. Margulis, M. A., Russian J. of Phys. Chem. 48(11), 1653(1974).

14. Chen, J. W.; Chang, J. A.; Smith, G. V., Chemical Engineering Progress Symposium Series, No. 109, Vol. 67, P.18.

15. Chen, J. W.; Kalback, W. M., Ind. Eng. Chem. Fund., 6, 175(1967).

16. Rozenberg, L. D., Soviet Physics-Acoustics, No. 1, Vol. 11, P. 110(1965).

17. Fogler, H. S.; Barnes, D., Ind. Eng. Chem. Fund., 7, 222(1968).

18. Tsang, W.; Hampson, R. F., "Chemical Kinetic Data Base for Combustion Chemistry", J. Phys. Chem. Ref. Data, 15(3), 1087-1279(1986).

19. "Rate Constants of Gas Phase Reactions", U.S. Department of Commerce, National Bureau of Standards, COM-72-10014.

20. Baulch, D. L., et al., "Evaluated Kinetic Data for High Temperature Reactions", J. Phys. Chem. Ref. Data(1981).

21. Johnston, H. S., "Gas Phase Reaction Rate Theory", Ronald Press Company, New York, 1966.

Table & Figure Captions:

Figure 1. Experimental Apparatus

Figure 2. Sonication Cell

Table 1. Proposed Chemical Kinetic Mechanism

Figure 3. $[CCl_4]$ Decrease Versus Sonication Time; $[CCl_4]$=130 ppm

Figure 4. $[CCl_4]$ Decrease Versus Sonication Time; $[CCl_4]$=47 ppm

Figure 5. $[CCl_4]$ Decrease Versus Sonication Time; $[CCl_4]$=8 ppm, 1.6 ppm, 0.53 ppm

Figure 6. First-Order Plot of $\ln[CCl_4]$ Versus Sonication Time

Figure 7. Effect of Steady-State Temperature on CCl_4 Sonication

Figure 8. Effect of Power Intensity on CCl_4 Sonication

Figure 9. Dependence of CCl_4 Destruction Rate on Power Intensity

Figure 10. Effect of Initial pH Value on CCl_4 Sonication

Figure 11. Effect of H_2O_2 Dosage on CCl_4 Sonication

Figure 12. Effect of H_2O_2 Dosage on CCl_4 with No Sonication

FIGURE 1. EXPERIMENTAL APPARATUS

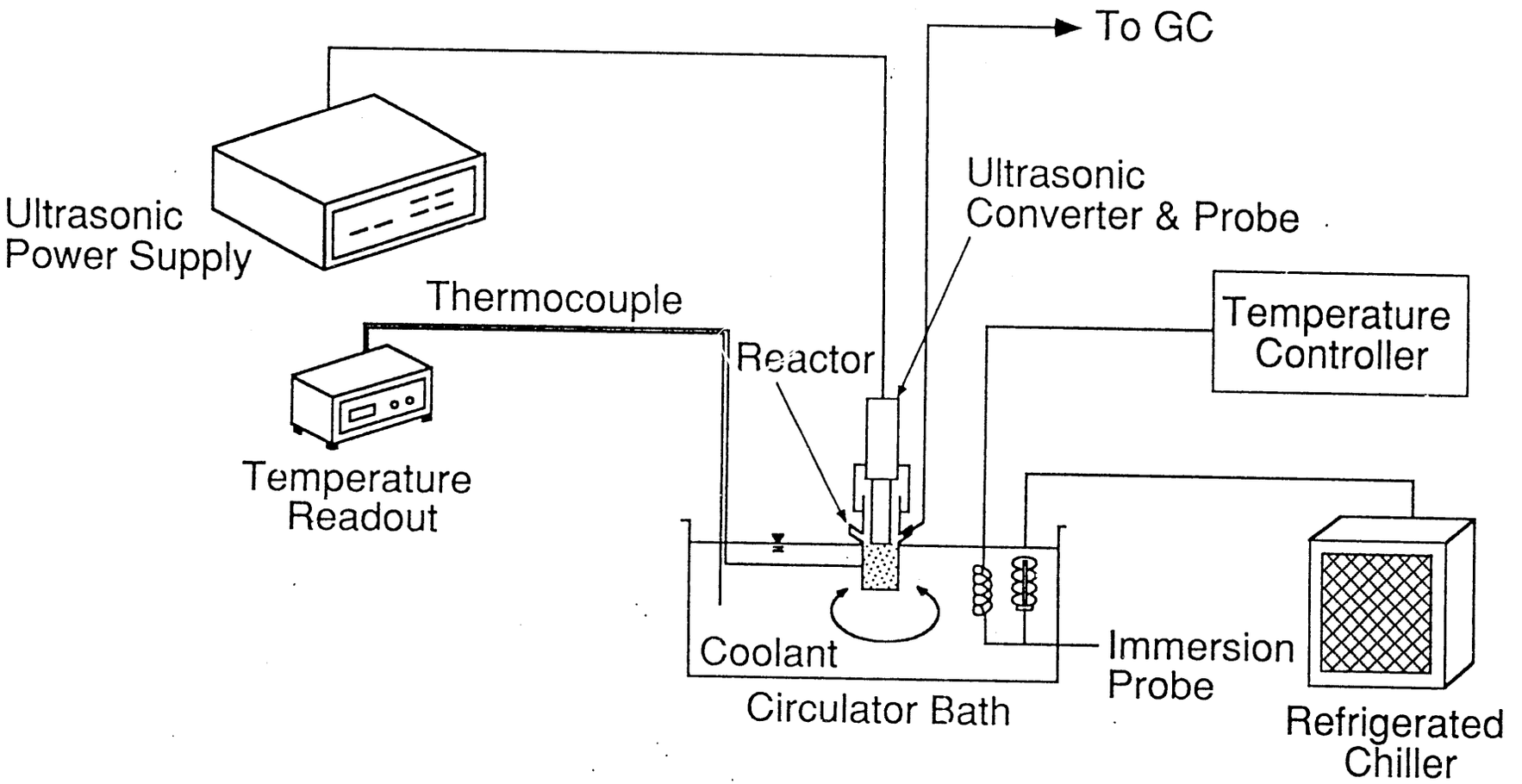


FIGURE 2. SONICATION CELL

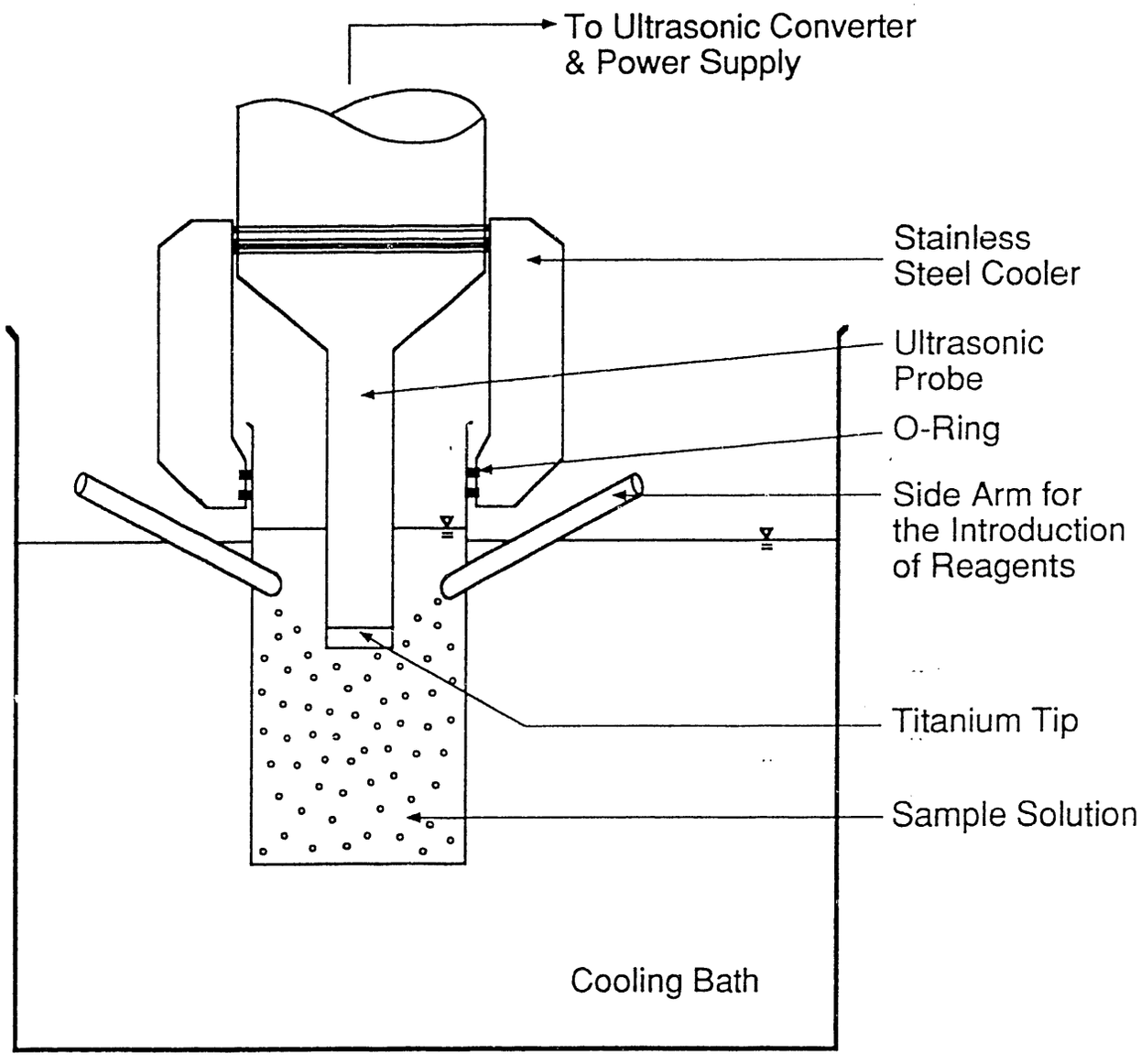


TABLE 1. PROPOSED CHEMICAL KINETIC MECHANISM

A. Water Dissociation:

1. H_2O —))) $H+OH$
2. $H+H \rightarrow H_2$
3. $H+O_2 \rightarrow HO_2$
4. $HO_2+HO_2 \rightarrow H_2O_2+O_2$
5. $OH+OH \rightarrow H_2O_2$
6. $H+OH \rightarrow H_2O$
7. $H+H_2O_2 \rightarrow OH+H_2O$
8. $H+H_2O_2 \rightarrow H_2+HO_2$
9. $OH+H_2O_2 \rightarrow HO_2+H_2O$
10. $OH+H_2 \rightarrow H_2O+H$

B. In the Presence of Nitrogen:

11. N_2 —))) $2N$
12. $N+OH \rightarrow NO+H$
13. $NO+OH \rightarrow HNO_2$
14. $NO+OH \rightarrow NO_2+H$
15. $2NO_2+H_2O_2 \rightarrow HNO_2+HNO_3$
16. $N+H \rightarrow NH$
17. $NH+NH \rightarrow N_2+H_2$
18. $N+O_2 \rightarrow NO+O$

TABLE 1 (cont'd)

C. In the Presence of Oxygen:

19. O_2 ——))) 2O
20. $H + O_2 \rightarrow OH + O$
21. $O + H_2 \rightarrow OH + H$
22. $O + HO_2 \rightarrow OH + O_2$
23. $O + H_2O_2 \rightarrow OH + HO_2$

D. In the Presence of Organics (CCl_4):

24. $CCl_4 + OH \rightarrow$ products
25. $CCl_4 + H \rightarrow$ products
26. $CCl_4 + HO_2 \rightarrow$ products
27. $CCl_4 + O \rightarrow$ products
28. CCl_4 —-))) products

FIGURE 3. $[CCl_4]$ DECREASE VERSUS SONICATION TIME; $[CCl_4]$ = 130 ppm

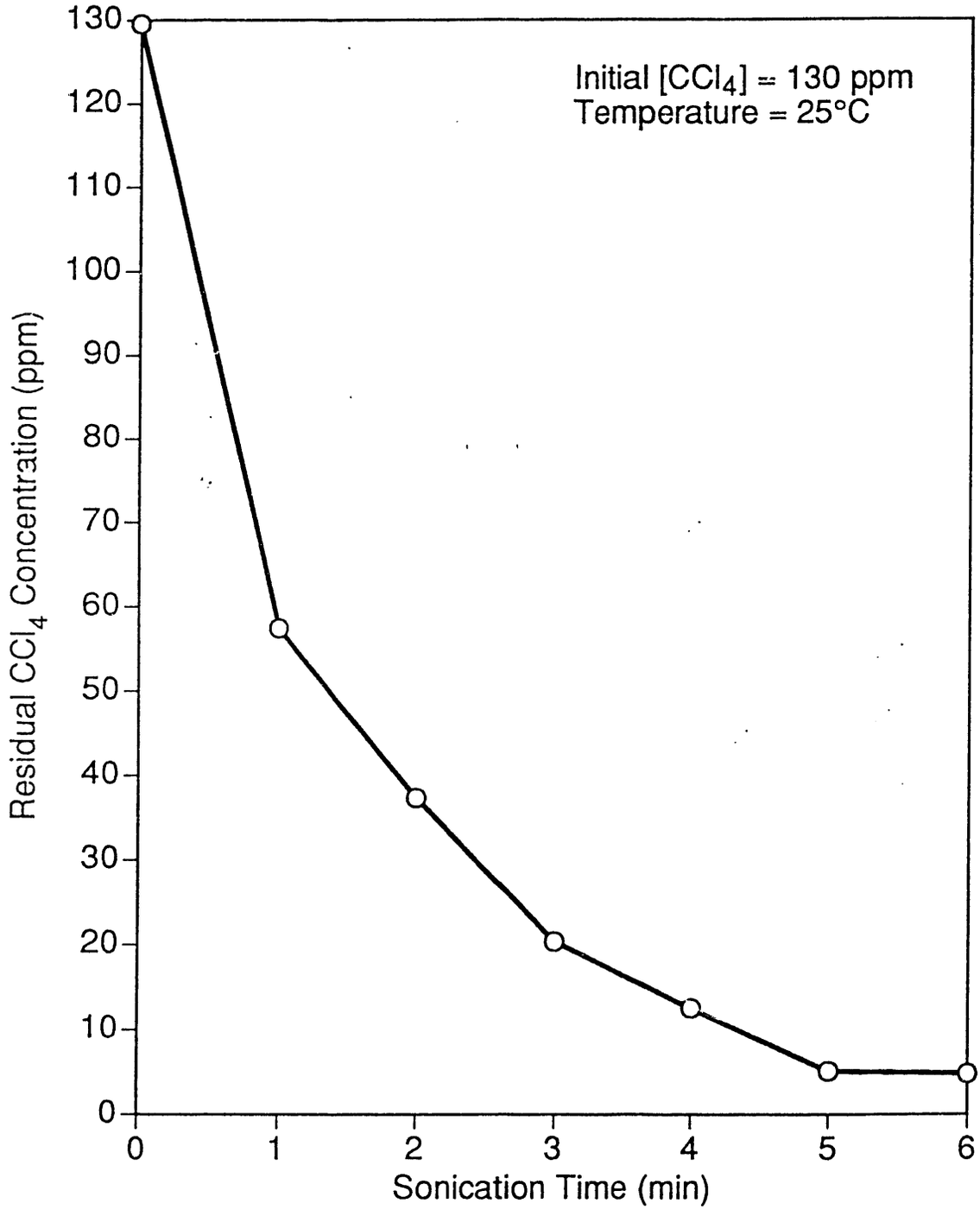


FIGURE 4. $[CCl_4]$ DECREASE VERSUS SONICATION TIME; $[CCl_4]$ = 47ppm

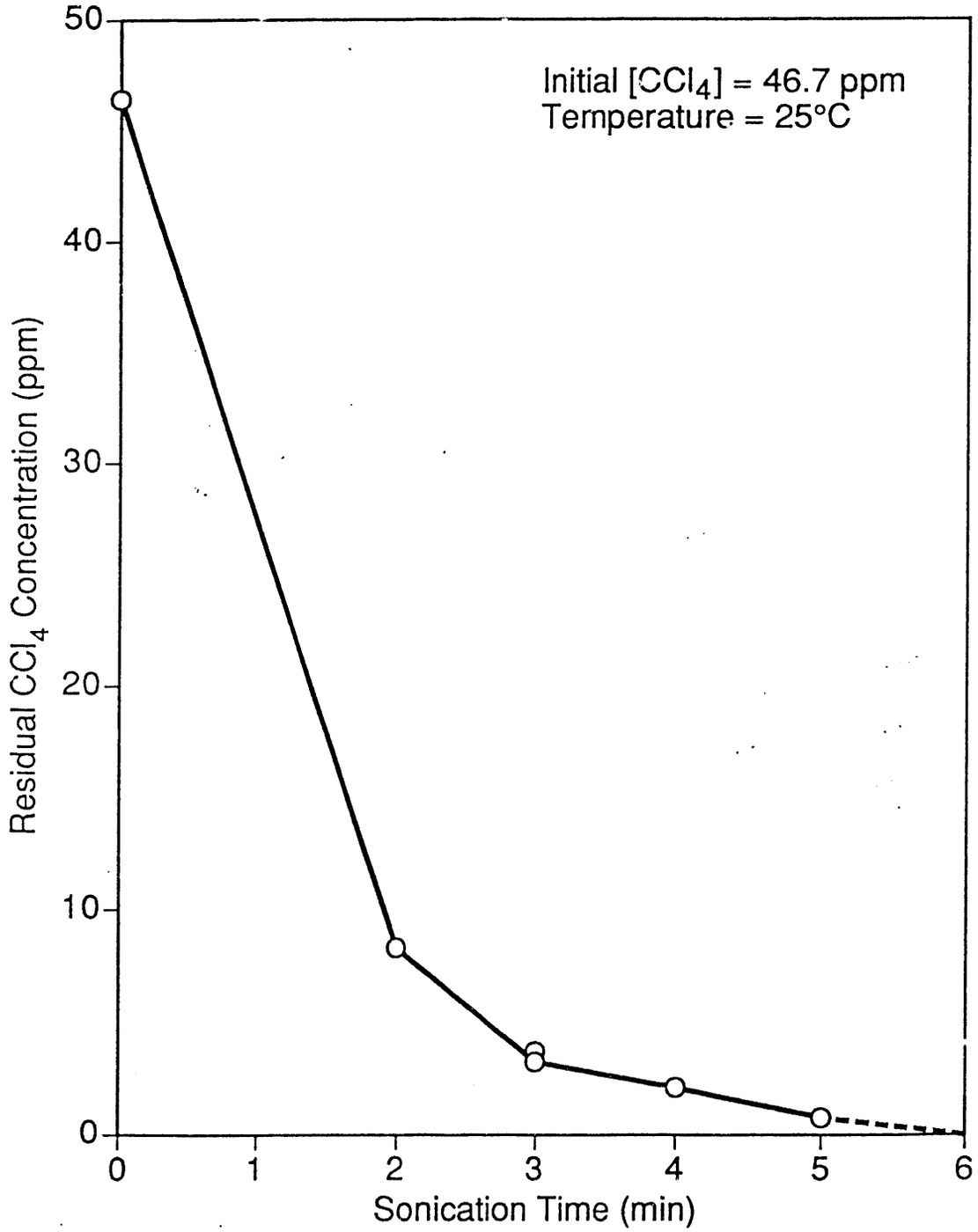
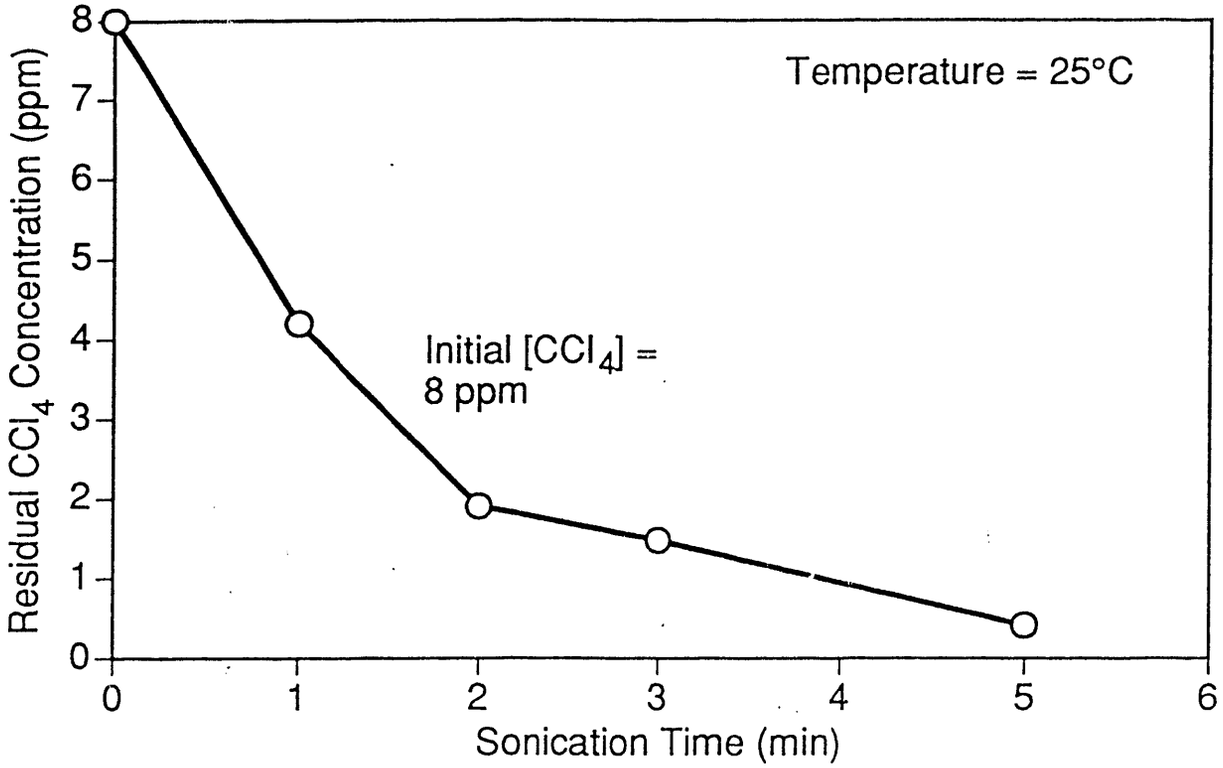


FIGURE 5. $[CCl_4]$ DECREASE VERSUS SONICATION TIME; $[CCl_4]$ = 8 ppm, 1.6 ppm, 0.53 ppm



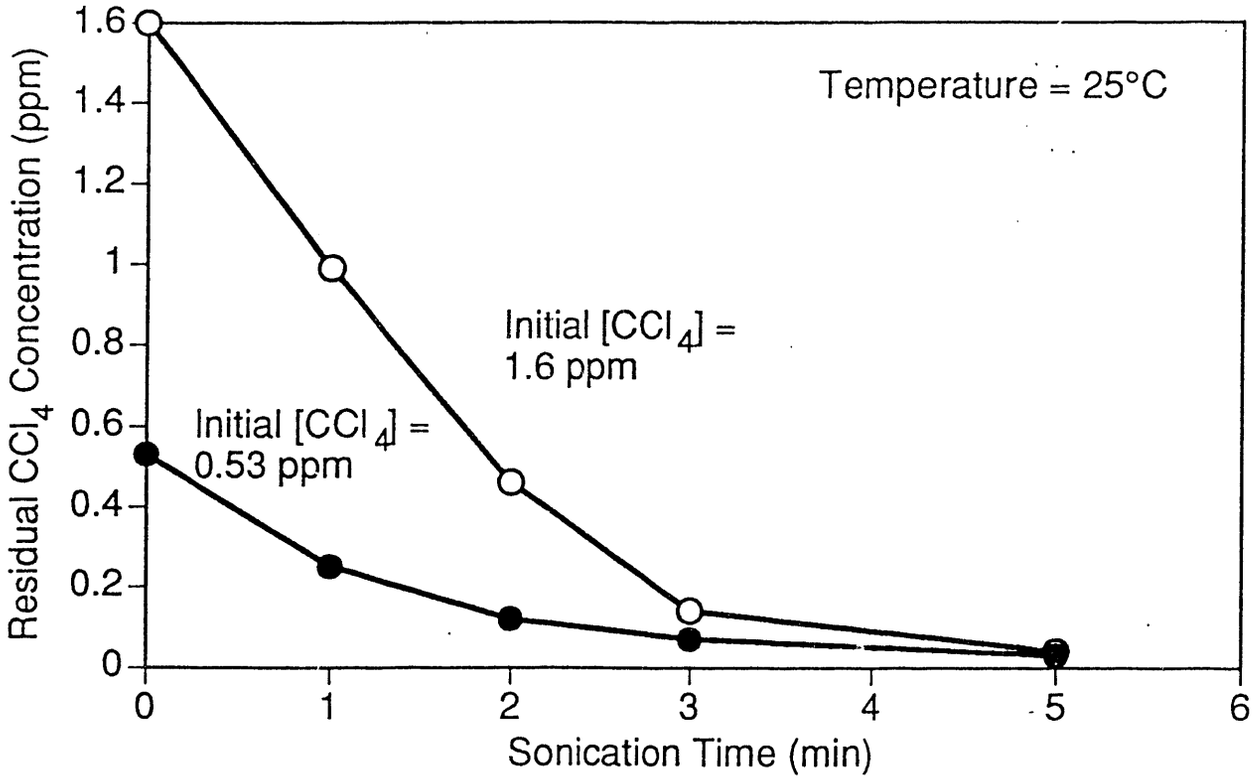


FIGURE 6. FIRST-ORDER PLOT OF ln $[CCl_4]$ VERSUS SONICATION TIME

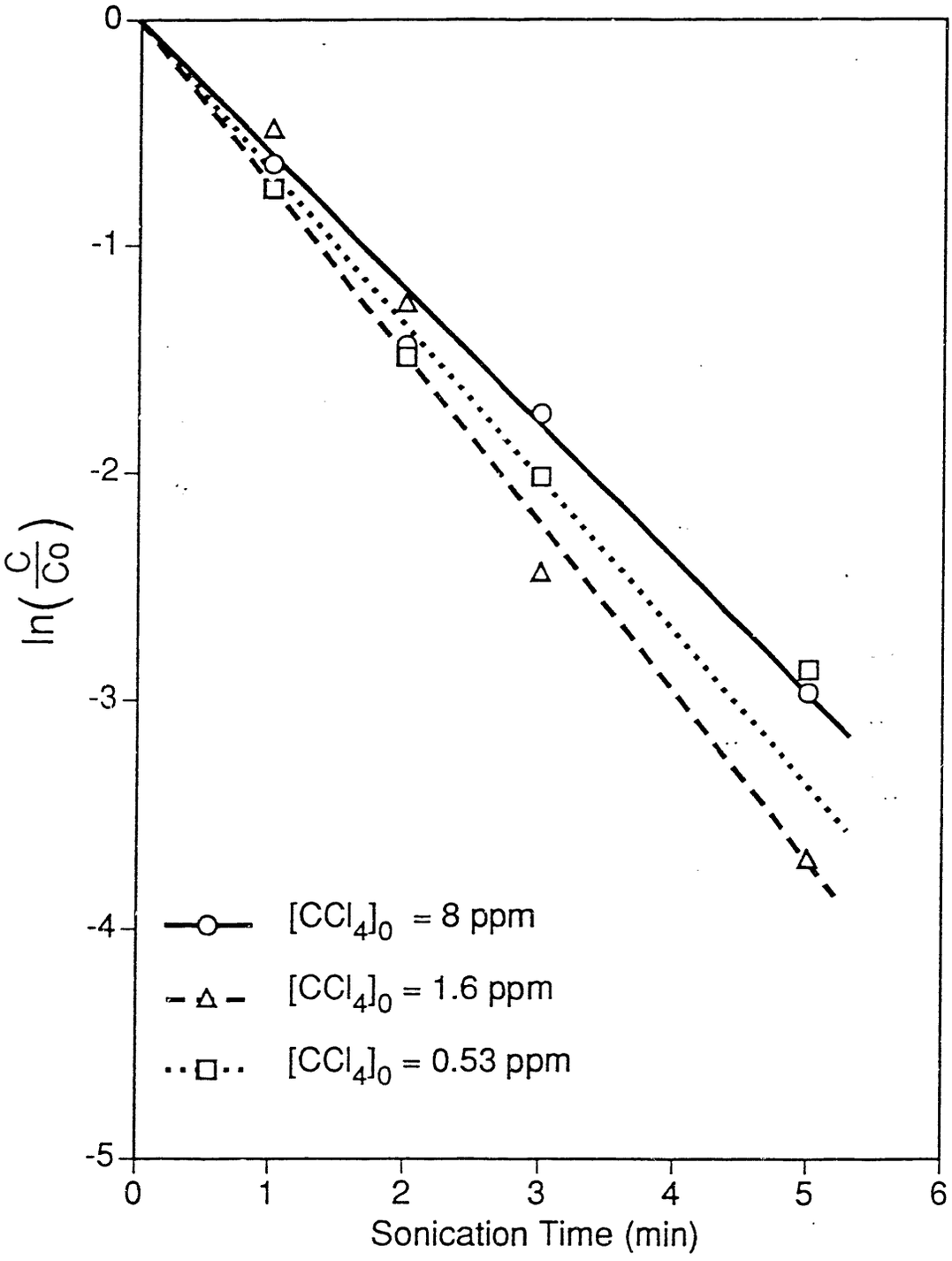


FIGURE 7. EFFECT OF STEADY-STATE TEMPERATURE ON CCl_4 SONICATION

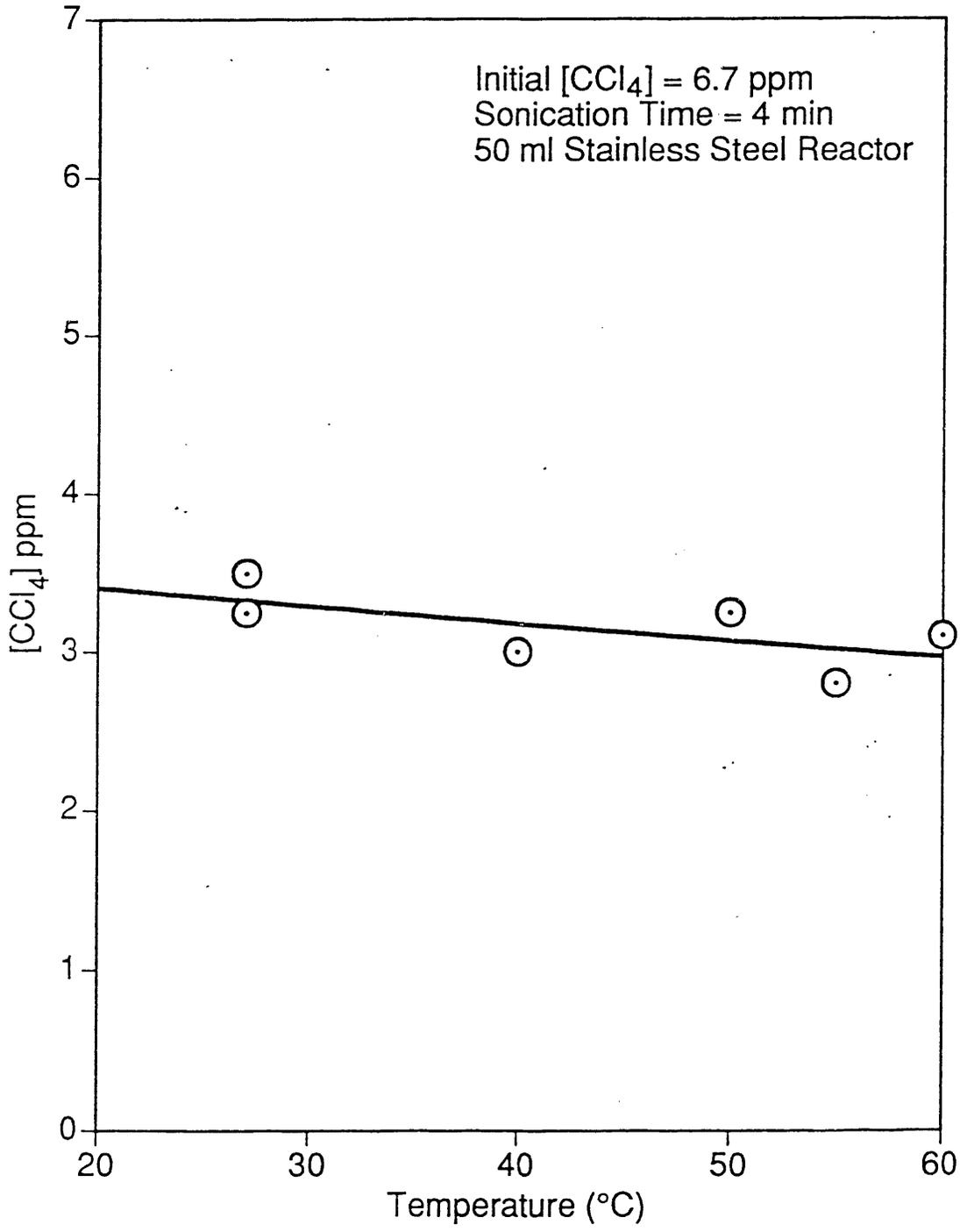


FIGURE 8. EFFECT OF POWER INTENSITY ON CCl_4 SONICATION

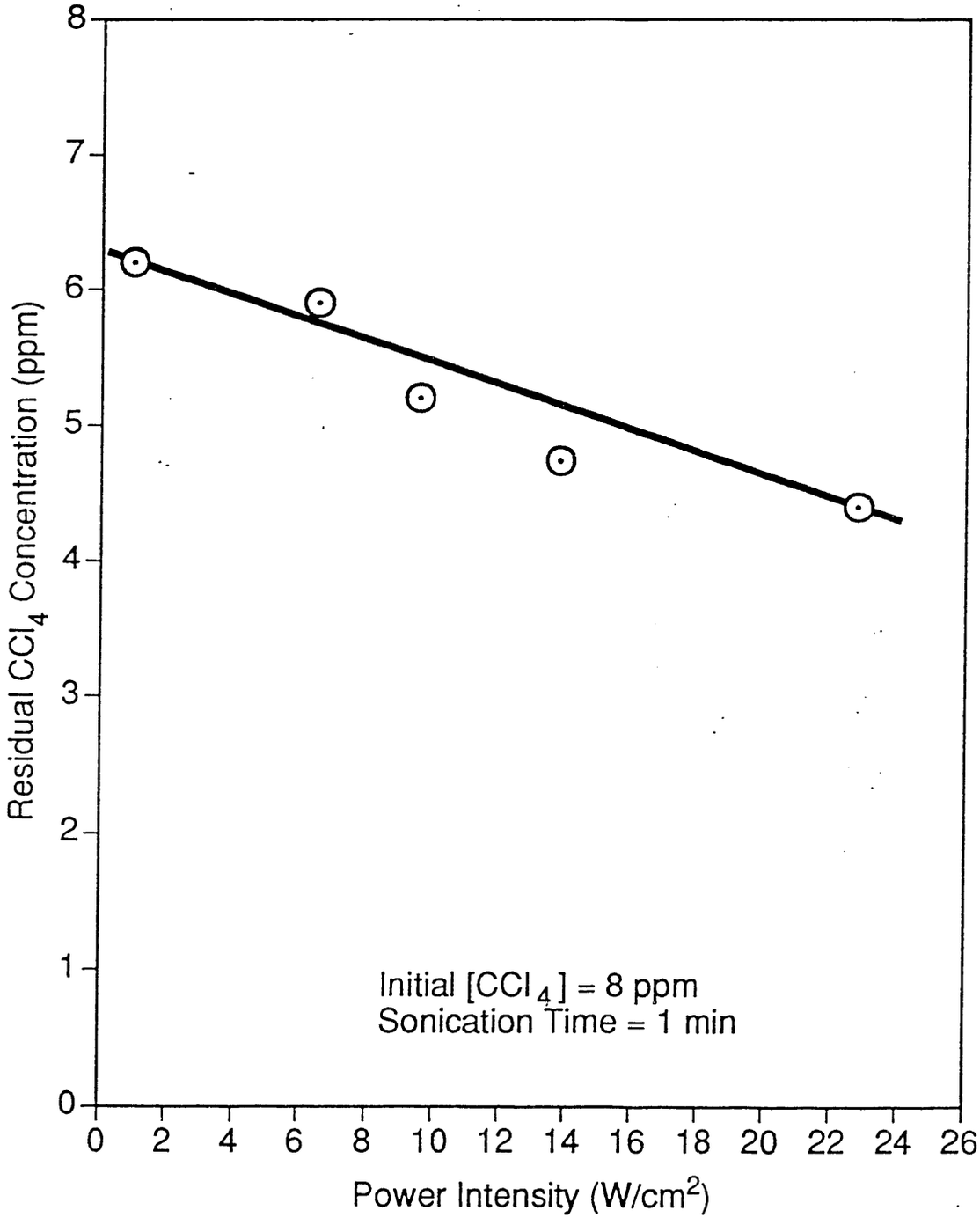


FIGURE 9. DEPENDENCE OF CCl_4 DESTRUCTION RATE ON POWER INTENSITY

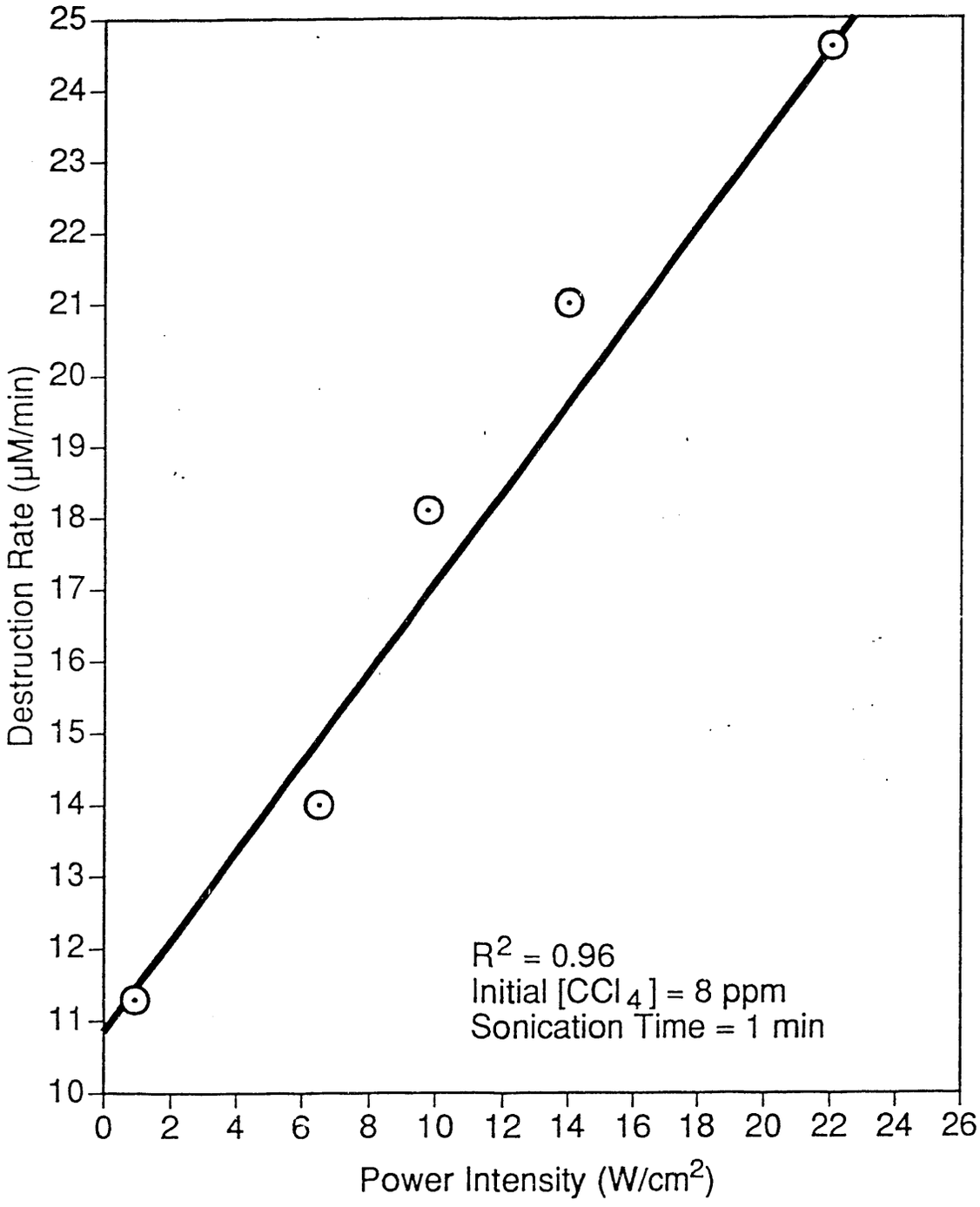


FIGURE 10. EFFECT OF INITIAL PH VALUE ON CCl_4 SONICATION

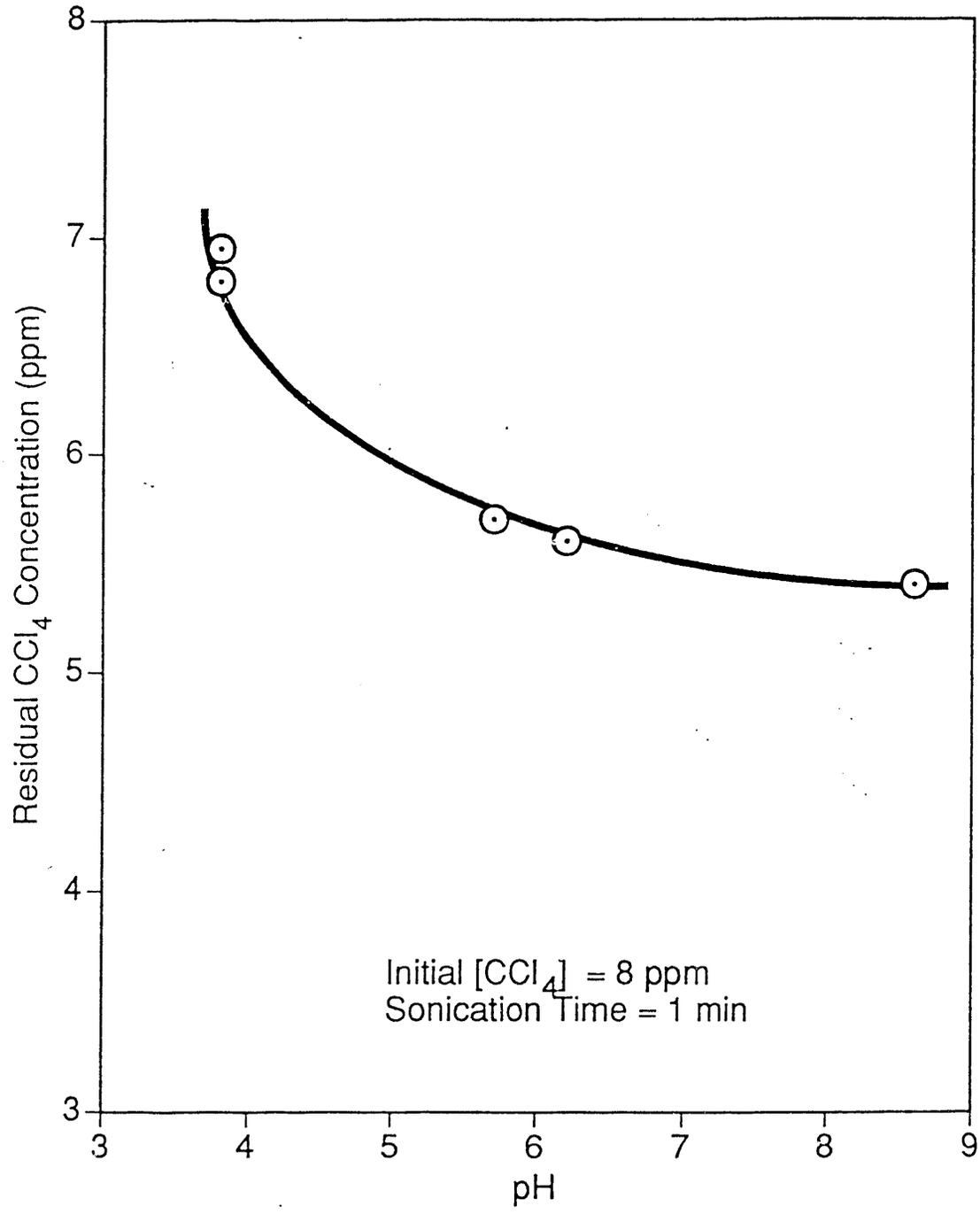


FIGURE 11. EFFECT OF H_2O_2 DOSAGE ON CCl_4 SONICATION

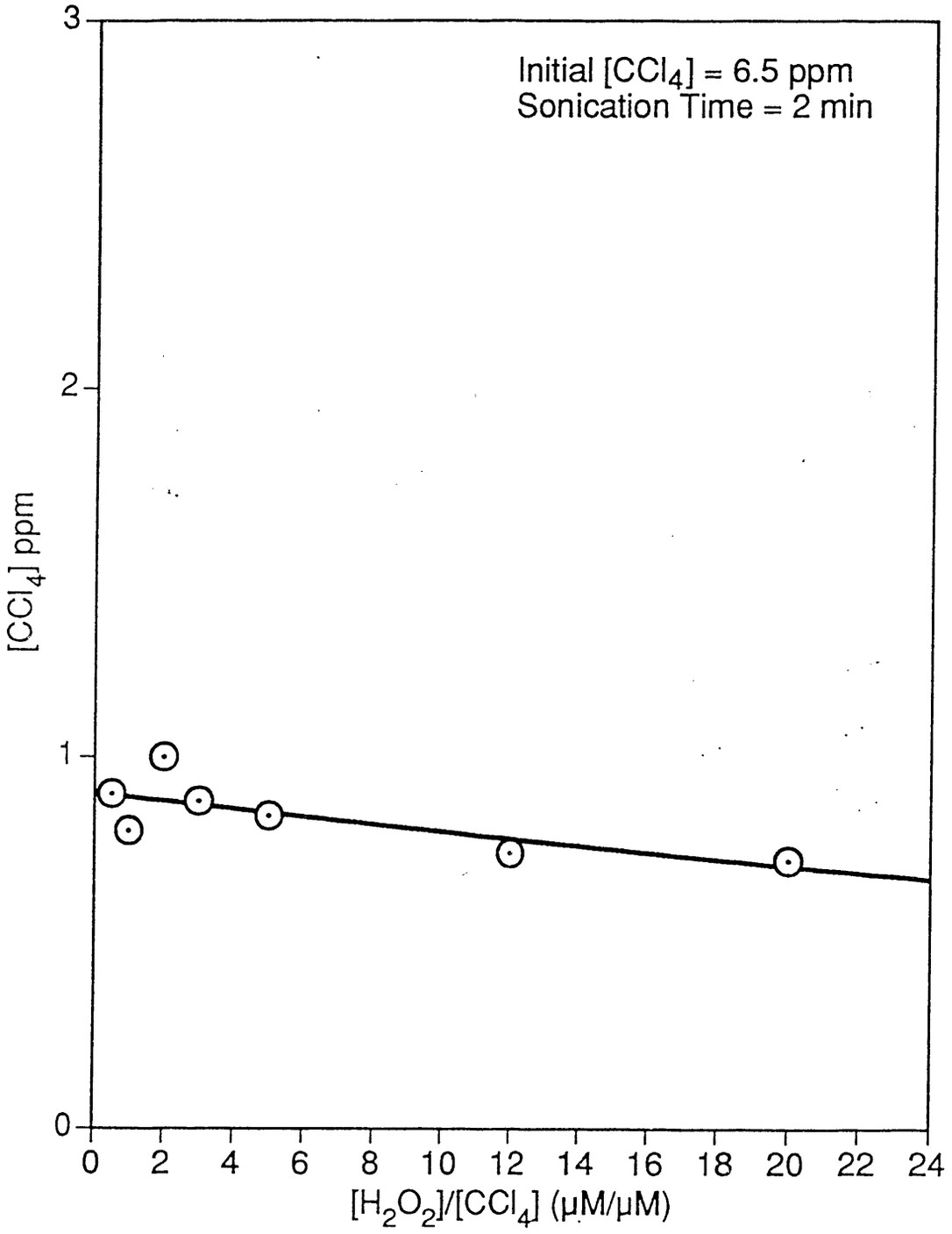
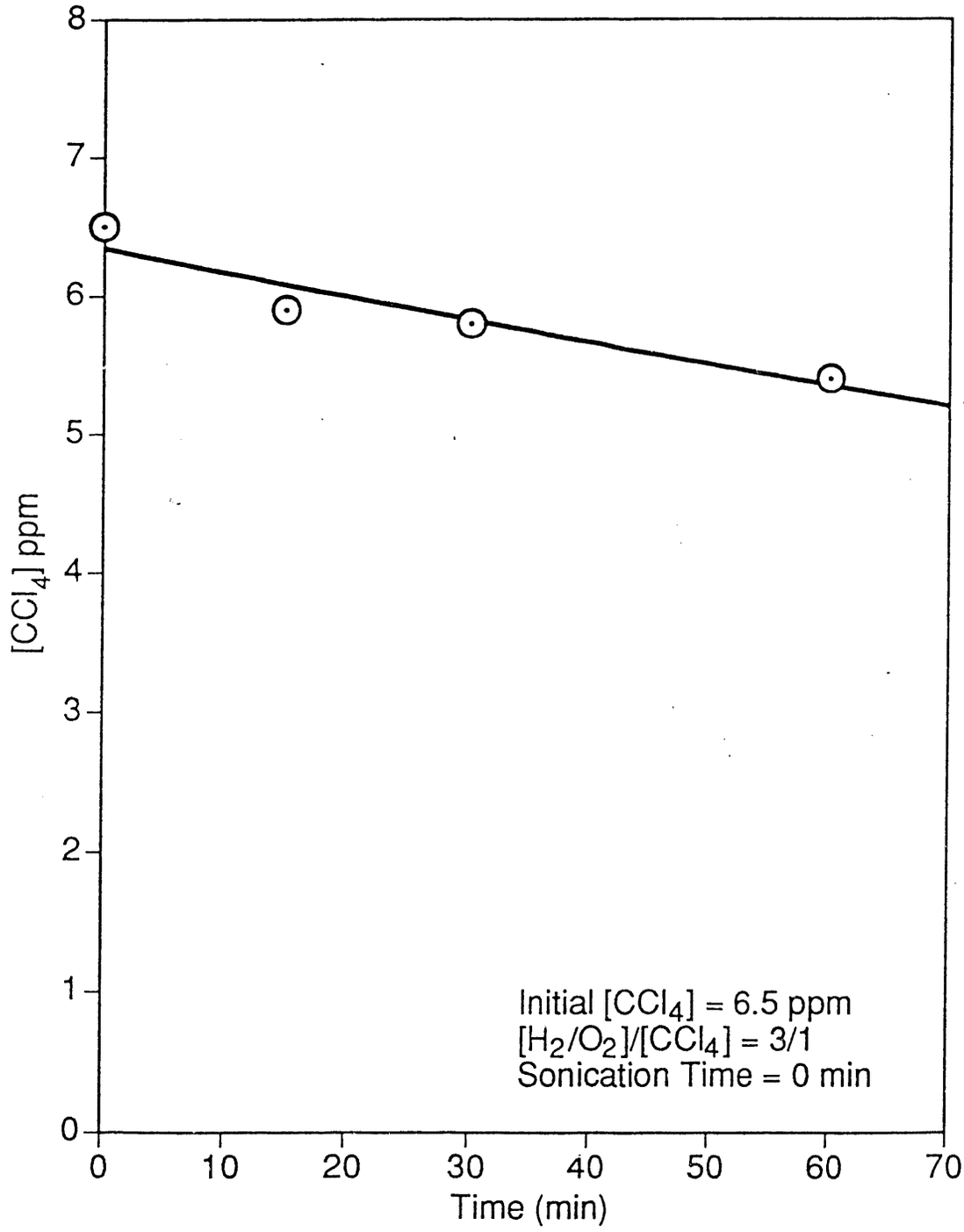


FIGURE 12. EFFECT OF H_2O_2 DOSAGE ON CCl_4 WITH NO SONICATION



END

DATE
FILMED
01/27/92